



## Electrodialytic remediation of CCA-treated waste wood

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Iben V. Christensen

Ph.D. Thesis, 2004

# Electrodialytic Remediation of CCA-Treated Waste Wood



Department of Civil Engineering  
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# Preface

The present Ph.D. thesis is submitted in completion of the requirements for the Ph.D. degree at the Technical University of Denmark. The work was done in the research group “Environmental Electrochemistry” Department of Civil Engineering, Technical University of Denmark, under supervision of Professor Arne Villumsen and Associate Professor Lisbeth M. Ottosen, both from Department of Civil Engineering, Technical University of Denmark.

I gratefully acknowledge all members of the Environmental Electrochemistry research group for creating an exiting and positive work environment and for their interest in my work. Special thanks to my good colleague and “office roommate” Anne Juul Pedersen for the valuable and brainy discussions we seemed to have on an almost daily basis. Lisbeth Ottosen, my supervisor and mentor are gratefully acknowledged for her support, wisdom and for being a cool professor ☺. Pernille Erland Jensen, Gunvor Marie Nystrøm and Inge Rörig -Dalgaard are acknowledged for stimulating inputs and good discussions. I wish to thank my supervisor Professor Arne Villumsen for supporting my work.

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I spent a week in Hamburg at the Federal Research Centre for Forestry and Forest products, Institute for Wood Biology and Wood Protection in connection with my Ph.D. I wish to thank Dr. Eckhard Melcher for his support and interest in my work. Dr. Uwe Schmitt kindly assisted in the interpretation of the results and the help by laboratory technician Tanja Potsch on the experimental work was invaluable.

During my Ph.D. I have had the privilege of meeting many different persons connected to the wood preservation industry. I especially want to thank Lars Nyborg, Osmose DK and Erik Borsholt for their support and interest in the project.

The financial contributions to parts of my work from The International Research Group on Wood Preservation, The Nordic Industrial Fund, The LIFE financial Instrument of the European Community and Otto Mønsted's Fond are greatly appreciated.

I also wish to acknowledge my good friend Malene Erkmann for providing the layout for the thesis and for her patience and support during the process.

My husband Willy Christensen and my mother Kirsten Horsbøl were invaluable especially during the final hectic phase of the process and I greatly acknowledge their support.

Iben Vernegren Christensen  
June 2004

# Summary

The service life of wood treated with CCA (chromated copper arsenate) may be 20 years or more due to the strong fixation of CCA in the wood. This has led to an extensive use of CCA-treated wood worldwide. The strong fixation however also means that a large proportion of the copper (Cu), chromium (Cr) and arsenic (As) is still present in the wood when it is removed from service and turns into waste. The content of As makes it a hazardous waste in many countries, including Denmark. The amount of impregnated waste wood is expected to increase dramatically and in Denmark alone it has been estimated that the amount of impregnated wood to be removed from service would increase from 17,000 tons in 1992 to 100,000 tons a year by 2010.

The aim of this thesis is to develop and optimise the Electrodialytic remediation (EDR) method to remediation of CCA-treated waste wood. The experiences obtained in this process are in the final part of the thesis discussed in the light of expanding the EDR method to other waste fractions.

Electrodialytic remediation (EDR) was originally developed for the removal of heavy metals from soil. The main principle behind EDR is that ions (including heavy metal ions) will move in an electric field and thereby be removed from the polluted material into liquids from where they can be collected. EDR uses a low voltage direct current as a cleaning agent and combines it with the use of ion exchange membranes to separate the electrodes from the polluted material (e.g. soil). In this thesis the polluted material is CCA-treated wood in the form of wood chips. An additive was used in order to facilitate the removal process and it was found to be most beneficial to soak the wood in the additive prior to EDR as opposed to using the additive directly in the EDR setup.

The fixation of CCA in wood during impregnation is a complex and not fully understood process. However in the found literature there is an agreement on the fact that the reduction of Cr(VI) to Cr(III) is the driving force of CCA fixation in wood. Cr oxidise sites in the wood that may serve as strong fixation sites for the fixation products. Cu is mainly expected to be fixed independent of As and Cr. As is proposed fixed mainly as chromium arsenate and the remaining Cr is proposed precipitated as chromium hydroxide.

In Denmark the softwood species Norway spruce and Scots pine are the most used for wood preservation. The structure of softwood is fairly simple compared to hardwood. Softwood consist of 90-95% tracheids, 5-10% rays and 0.1-1 % resin canals.

In the found literature CCA is generally found to be distributed in all parts of the wood. There is a clear tendency to higher concentrations of CCA in the ray cells



compared to the tracheids. This is in agreement with rays being the main penetration pathway for CCA.

Studies from the literature show that part of the CCA is leached from the wood during the service life but the use of a more balanced CCA formulation and the use of water repellent have decreased leaching during use. In general Cr was found to be the most leach resistant of the CCA-components. Several investigations have been made on the subject of actively extracting the CCA from the wood, in order to solve the increasing waste problem. CCA was reported to be removed to a large extend by different acids and complexing agents. Biological extraction by fungi and metal tolerant bacteria was also able to remove CCA.

In the experimental work done in this thesis, wood from a CCA-treated out of service pole and a mix of impregnated waste wood was used.

The optimization of the Electrodialytic remediation method in laboratory scale was primarily focussed on identifying the most suitable additive for the removal of Cu and Cr since these metals seemed to be more difficult to remove than As. Remediation at high pH was not successful, presumably due to precipitation of Cr and Cu at alkaline pH.

It was not possible to locate one additive that was ideal for removal of both Cu and Cr. In an acid environment it was found that the most suitable additive for Cr was oxalic acid, whereas phosphoric acid proved to be best suited for the removal of Cu. Prior to EDR the wood was soaked in the two additives.

In the laboratory scale it was possible to remove 92% Cu and 83% Cr from a batch of 70 g wood and the average residual concentrations in the wood was 102 ppm Cu and 232 ppm Cr.

SEM analyses of partly remediated wood showed no indications of a specific CCA-wood bonding that was not influenced by EDR. After soaking Cu and Cr was found to be present partly as precipitates on the lumen surfaces of the wood. After EDR the appearance seemed to be reduced in both tracheids and rays.

The EDR process was subsequently up scaled to a pilot scale that could remediate 0.3 – 2 m<sup>3</sup> wood at a time by varying the distance between the electrodes. In an experiment with approximately 100 kg wood the removal efficiency was as good as in the laboratory. The final concentrations in the wood was 163 ppm Cu, 252 ppm Cr and less than 43 ppm As. Further upscaling resulted in reduced removal of Cu and Cr, but in the only other experiment that was analysed for As approximately 250 kg wood chips was remediated and the final concentration of As was less than 33 ppm. There was a clear tendency of decreased removal of CCA with increasing wood size fraction and increasing distance between the electrodes but at least the influence by distance is supposed to be diminished by the use of a stronger power supply.

Investigations in the laboratory showed that the presence of minor amounts of metallic metal pieces (like iron nails and copper wire) in the wood chip batches did not influence the remediation process significantly and makes the chipping and sorting of waste wood possible by commercial methods (shredding and magnetic separation of metallic metal pieces). This is very encouraging if EDR is to be used in larger scale.

The usability of the wood after remediation was investigated. If the wood is to be reused after the removal of CCA, the influence of oxalic acid on the strength of the wood may be important.

Investigations of the influence of oxalic acid on bending strength of pine wood revealed no significant difference in the bending strength due to oxalic acid or EDR.

The process liquids from EDR were investigated for the direct use in impregnating new wood by CCA. The results showed that pre-treatment of the liquids were necessary before they could be reused.

The results and experiences that was gained in the optimization process, both in the laboratory and in the process of up scaling EDR to pilot scale may be used in the evaluation of other materials to be remediated with EDR.

The most important characteristics of the polluted material is that the pollutant is to be present as ions in order to be removed by EDR. Identifying a suitable additive for the removal of the pollutants seems to be a key parameter and should be optimized with respect to concentration and pH, this may be done mostly by extraction experiments, but EDR experiments are needed in order to verify the suitability of the additive.

Through EDR experiments the current density, optimum duration of the experiments, liquid to solid ratio are to be investigated. After optimising the EDR process in the laboratory, the up scaling may begin. In the large scale parameters including electrode distance, the use of collecting units and the membrane area are to be investigated. If the up scaling was successful, further up scaling to eventually industrial scale is possible.

In the case of CCA-treated wood, the up scaling of EDR to pilot scale was very promising. It was possible to remove almost all As which is the CCA component of most concern. The concentration of Cu and Cr was reduced to less than half of the initial concentration and further reduction can most likely be achieved with the use of a stronger power supply.

# Dansk sammendrag

Træ der er imprægneret med CCA (chromated copper arsenate) har ofte en levetid på 20 år eller mere på grund af den effektive fiksering af CCA i træ. Det har betydet at brugen af CCA har været udbredt i store dele af verden. Den gode fiksering af CCA i træet betyder også at en stor del af det oprindelige kobber (Cu) chrom (Cr) og arsen (As) fra CCA stadig er i træet når det ender som affald. Når træet indeholder arsen klassificeres det som farligt affald i mange lande, inklusiv Danmark. Mængden af imprægneret affaldstræ forventes at stige væsentligt i de nærmeste år. Alene i Danmark forventes mængden at stige fra 17.000 tons i 1992 til 100.000 tons imprægneret affaldstræ per år fra 2010.

Formålet med denne afhandling er at udvikle og optimere den elektrodialytiske rensningsmetode (EDR) så den kan bruges til at fjerne CCA fra imprægneret affaldstræ. De erfaringer og resultater der opnås i denne proces vil i den afsluttende del af nærværende rapport blive diskuteret og evalueret i forhold til at udvide EDR metoden til rensning af andre affalds fraktioner.

Elektrodialytisk rensning (EDR) blev oprindeligt udviklet som metode til at fjerne tungmetaller fra forurenede jord. Princippet bag EDR er at ioner (inklusive tungmetallioner) vil bevæge sig i et elektrisk felt. Derved kan tungmetallerne fjernes fra jorden og opsamles i væsker hvorfra de kan genindvindes. Udover den elektriske jævnstrøm benytter EDR også ionbyttemembraner til at adskille jorden fra elektroderne. I denne afhandling metodens anvendelighed undersøgt i forbindelse med at fjerne CCA fra imprægneret affaldstræ som træflis. Et additiv blev brugt for at gøre det nemmere at fjerne Cu, Cr og As. Det viste sig at være bedst at lægge træet i blød i additivet før rensningen med EDR, i stedet for at tilsætte additivet til træet under selve rensningen.

Fikseringen af CCA i træ under imprægneringen er en kompleks proces, som ikke er fuldt forstået. Der er dog enighed om at reduktion af Cr(VI) til Cr(III) er drivkraften i fikseringsprocessen. Cr oxiderer dele af træet og der dannes sites hvor CCA kan fikseres. Størstedelen af Cu bindes direkte til træet, uafhængigt af Cr og As. As fikseres sandsynligvis som chromarsenat mens det overskydende Cr udfælder som chromhydroxid.

I Danmark er nåletræerne Rødgran og Skovfyr de mest benyttede træarter når det gælder imprægnering. Nåletræers opbygning er rimelig simpel sammenlignet med løvtræ. Nåletræer består af 90-95% trakeider, 5-10% marvstråle celler og 0,1-1% harpiks kanaler.

I litteraturen findes eksempler på at CCA generelt er fordelt i alle dele af træet. Der er en klar tendens til højere koncentrationer af CCA i marvstrålerne sammenlignet med

trakeiderne. Det er i overensstemmelse med at CCA primært trænger ind i træet gennem marvstrålerne.

I litteraturen findes der flere eksempler på at CCA udvaskes fra træet under brug, men efter at man er gået over til en mere afbalanceret CCA blanding suppleret med brugen af vandafvisende midler er udvaskning af CCA under brug reduceret. Generelt er Cr den af de tre CCA komponenter der udvaskes mindst. Der findes mange eksempler på at man har forsøgt aktivt at ekstrahere CCA fra træ i forsøget på at løse det stigende affaldsproblem. Store dele CCA er blevet ekstraheret med forskellige syrer og kompleksdannere. Biologisk ekstraktion med fungi (svampe) og metal-tolerante bakterier er også i stand til at fjerne en del af CCA fra træ.

I det eksperimentelle arbejde der er udført i denne afhandling blev der brugt træ fra en kasseret elmast og et mix af forskelligt imprægneret affaldstræ.

Under optimering af den elektrodialytiske rensningsmetode i laboratoriet blev der primært fokuseret på at finde et egnet additiv til at fjerne Cu og Cr fra træ, da disse metaller synes at være sværere at fjerne end As. Rensning ved basisk pH var ikke vellykket, sandsynligvis fordi Cr og Cu udfælder ved basisk pH.

Det var ikke muligt at finde et additiv der var velegnet til at fjerne både Cu og Cr. I surt miljø var oxalsyre det mest egnede additiv til at fjerne Cr, mens fosforsyre var det mest egnede til at fjerne Cu. Før EDR blev træet lagt i blød i de to additiver.

I laboratoriet var det muligt at fjerne 92% Cu og 83% Cr i et rensningsforsøg med 70 g træflis. Koncentrationen af Cu og Cr i træet efter rensning var 102 ppm Cu og 232 ppm Cr.

SEM analyser i delvist rensset træ vidste ingen tegn på at der var specifikke CCA-træ bindinger som ikke blev påvirket af EDR. Efter iblødlægning af træet var Cu og Cr at finde i træet som delvist udfældede på overfladen af cellerne i træet. Efter EDR var antallet af udfældninger formindsket både i trakeider og marvstråler.

Den elektrodialytiske rensningsmetode blev efterfølgende opskaleret og der blev bygget et pilotanlæg hvor der kunne renses mellem 0,3 og 2 m<sup>3</sup> træ ad gangen, ved at justere afstanden mellem elektroderne. I et forsøg med næsten 100 kg træflis var rensningsgraden lige så god som i laboratoriet. Efter rensning var der 163 ppm Cu, 252 ppm Cr og mindre end 43 ppm As tilbage i træet. Yderligere opskalering resulterede i dårligere rensning af Cu og Cr, men i det eneste andet forsøg hvor As blev målt, var koncentrationen efter rensning mindre end 33 ppm og her blev der rensset i alt 250 kg træ flis. Der var en klar tendens til formindsket rensning af Cu og Cr med stigende størrelse af træflisen og stigende afstand mellem elektroderne, som dog forventes at kunne blive løst ved at benytte en større strømforsyning.

Undersøgelserne i laboratoriet viste efterfølgende at tilstedeværelsen af små mængder metal stykker i træflisen ikke havde betydning for rensningseffektiviteten. Det betyder

at industrielle tilgængelige metoder kan bruges til at neddele og fjerne det meste metal ved at køre træet over et magnetbånd. Det er en fordel hvis metoden skal bruges i industriel skala.

Muligheden for at genanvende træet efter rensning blev undersøgt. Hvis træet skal genbruges kan det være en fordel at undersøge om EDR eller additiver som oxalsyre har nogen indflydelse på træets styrkeegenskaber. Undersøgelser viste at hverken oxalsyre eller EDR synes at have indflydelse på bøjningsstyrken af fyrretræ.

Det blev ligeledes undersøgt om proces væskerne fra EDR kunne bruges direkte til at imprægnerer nyt CCA imprægneret træ, men det viste sig at en form for forbehandling var nødvendig før de kunne anvendes.

Resultaterne og erfaringerne som var opnået under optimeringsprocessen, både i laboratoriet og i pilot skala forventes at kunne danne baggrund for vurderingen af om andre materialer kan renses med EDR.

Det vigtigste karakteristika ved det forurenede materiale som skal renses er at forureningen er på ionform, da det er ioner der kan fjernes med EDR. At finde et egnet additiv synes også at være en nøgle parameter både pH og koncentration af additivet skal optimeres. Dette kan for en stor del gøres med ekstraktions forsøg, men EDR forsøg er nødvendige for at bekræfte anvendeligheden af additivet til EDR. Optimal strøm-tæthed, rensningens varighed og L:S forholdet skal bestemmes på baggrund af EDR rensnings forsøg. Efter EDR er optimeret i laboratoriet, kan opskaleringen begynde. I større skala kan parametre som elektrode afstand, brugen af opsamlingskamre og membranarealets indflydelse undersøges og optimeres. Hvis opskaleringen til pilot anlæg er en succes, kan videre opskalering eventuelt til industriskala være mulig.

Opskaleringen af rensning af træ imprægneret med CCA fra laboratorieskala til pilotskala var vellykket. Det var muligt at fjerne stort set al As som er den del af CCA der giver anledning til størst bekymring. Koncentrationen af Cu og Cr blev reduceret til under halvdelen af det oprindelige og det vil sandsynligvis være muligt at fjerne endnu mere når der anvendes en større strømforsyning.

# Introduction

## 1. CCA-treated waste wood

The wood preservative Chromated Copper Arsenate (CCA) has been used worldwide since the 1950s. It is accepted as one of the most effective treatments for the protection of wood against fungi, insects and marine borers (*Eaton & Hale 1993*). The service life of wood impregnated with CCA may be 20-50 years or even more (*Cooper et al. 2001a*) implying good fixation of the CCA in the wood.

The good fixation of CCA in wood is also the reason CCA-treated wood becomes a problematic waste fraction when it is removed from service. Even though some leaching will occur during use, the good fixation will result in often high concentrations of the CCA components: copper (Cu), chromium (Cr) and arsenic (As), in the wood when it eventually ends up as waste wood (*Cooper et al. 2001b*). These metals may enter into the waste stream unless actions are taken to prevent this.

CCA was used extensively in Denmark from the late 1950s until 1993, when the use of As for wood preservation was banned. (*Hansen et al. 1997*)

### 2.1 Legislation for use of CCA in Denmark

The replacements for CCA in Denmark included Cr, Cu and Boron formulations and/or organic formulations. Cr was used until 1997, where the use of Cr in wood preservative formulations has been very limited in Denmark after the wood preservers made a voluntary agreement with the environmental authorities to phase out Cr. It is still possible to buy imported wood treated with Cr in Denmark, but import of wood that was treated with As is forbidden. (*Miljøstyrelsen 2004*).

However an EC directive (2003/2/EC) relating to restrictions on the marketing and use of arsenic will come into force in the end of June 2004. The purpose of the directive is to restrict the use of CCA, but since the use of CCA has been banned totally in Denmark, the directive could have the opposite effect in Denmark.

According to the directive CCA-treated wood may then no longer be used in residential or domestic constructions or in marine waters. CCA-treated wood may only be used in industrial applications provided that the structural integrity of the wood is required for human or livestock safety and the skin contact by the general public during its service life is unlikely. Denmark has implemented the directive (*BEK nr. 536 af 18/06/2003*) and as a consequence, the 10 year old total ban of CCA in Denmark is lifted.

It is unknown to what extent CCA will be used in Denmark as a result of the new

directive, but no dramatic increase is expected according to Miljøstyrelsen (Danish EPA)(*Bjørnsen 2004*).

At present no CCA formulations is permitted for use in Denmark and therefore an application to Miljøstyrelsen are required on an individual basis in order to allow the use of CCA treated wood. According to the text of the directive, the applicants have to justify the need for CCA, by danger involved for human or livestock safety if CCA treated wood is not used. Since other preservative formulations have been used instead of CCA in the recent 10 years, it seems unlikely that the required need for CCA will be met.

In U.S.A. the use of CCA has also been restricted and is no longer allowed for residential uses (e.g. picnic tables, play structures etc.). This restriction came into force in 2004.

Restrictions on the use of CCA-treated wood is primarily due to the content of As and the risk of As leaching during use. Therefore CCA is in general restricted to industrial use and banned in places where the public may come into (skin) contact with CCA-treated wood.

These restrictions will also restrict the amount of waste wood, however the long service life of CCA-treated wood will result in the presence of CCA-treated waste wood in many years to come.

## 2.2 Legislation for waste wood

The content of arsenic makes CCA-treated waste wood a hazardous waste according to the Danish legislation and the local councils have to assign disposal possibilities for the impregnated wood as well as systems for separate collection (*BEK nr. 619 af 27/06/2000*).

Incineration of CCA-treated wood is banned in Denmark and deposition of the wood in special landfills is the only alternative until new methods has been developed that ensures the utilization of both the energy resource and the metals in the impregnated wood (*Affald 21, 1999*)

## 2.3. Enforcement of the Danish legislation in practice.

In practice the collection of impregnated wood is taking place at local public recycling centers. At some recycling centres the impregnated wood is collected in containers together with other materials classified as not suitable for incineration e.g. PVC and asphalt. At a few recycling centres a special container for impregnated wood is present, but this is not required.

It may be very difficult to sort out the impregnated waste wood in practise. Wood impregnated with Cu (including CCA) has a characteristic green colour, but after several years in service the wood may appear grey, and look similar to untreated weathered



wood.

As aid for sorting out impregnated wood Miljøstyrelsen has produced a handbook that provides an overview of various types of impregnated and non-impregnated wood. The book, which is intended for the staff at recycling centres, describes in words and pictures the visual characteristics and typical use of impregnated and non-impregnated wood. The book also explains that impregnated wood should be collected and managed separately at the recycling centres.

At present sorting is done on basis of visual inspection and knowledge on use of the specific wood. Meanwhile, a sensor for detection of heavy metals in wood has been developed by DK-teknik and Force in Denmark. (*Cramer 2004*) The sensor can distinguish between different inorganic wood preservatives and can thus be used for separation of salt impregnated wood into a hazardous and a non-hazardous fraction. The sensor is stationary and developed for use at recycling centres. Whether the sensor will be used for sorting of impregnated waste wood is uncertain at present since the methods that are under development for handling the wood waste can handle a mix of impregnated and un-impregnated wood. The sensor can be used for sorting PVC out from other plastic as well, and here the use is considered to be more promising than for sorting wood by the inventors of the sensor.

## 2.4. Amount of waste wood

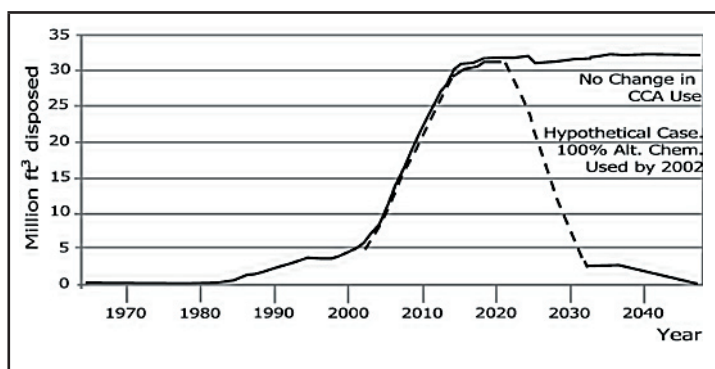
The amount of impregnated waste wood is expected to increase dramatically in the present years. It has been estimated by Miljøstyrelsen that the amount of impregnated wood removed from service would increase from 17,000 tons in 1992 to 100,000 tons a year by 2010. Furthermore it was estimated that in total 2.7 million tons of impregnated waste wood has been used in Denmark since the 1960s and this wood will eventually turn up as waste. (*Affald 21, 1999*)

A newer estimate of the amount of impregnated waste wood in Denmark, based on production as well as import and export data, amounts the impregnated wood to approximately 4 million tons. The investigation does not take degradation and uncontrolled combustion of impregnated wood into account (*Andersson & Quistgaard 2002*).

Similar trends can be seen in other countries. In Norway an increase in the amount of impregnated waste wood is estimated to be from below 200,000 tons in the present decade, to more than 1.6 million tons in the years 2041-2050. (*Evans 2001*)

In figure 1 a long-term disposal forecast for Florida, U.S.A. predict that the amount of CCA-treated waste wood will increase from below 5 million ft<sup>3</sup> in the 1990s to 30 million ft<sup>3</sup> in 2015 (*Solo-Gabriele & Townsend 2000*).





**Figure 1:** Long-term disposal forecast for CCA-treated wood waste in Florida. (Adapted from *Solo-Gabriele and Townsend 2000*)

The restrictions on the use of CCA will of course lead to a reduction in CCA-treated waste wood, but due to the long service life of CCA-treated wood, the expected decrease in waste will only become apparent much later (see figure 1).

### 3. Solving the problem of CCA treated waste wood

Different attempts to reuse or recycle CCA treated wood will be summarized here, based on a literature survey.

An extensive analysis of consumer lumber waste management options was made recently by *Cooper et al. (2001a)*. *Helsen & Van den Bulck (2004)* has extended the survey to cover thermochemical conversion processes as disposal options for CCA treated wood waste. Here the most important options are briefly addressed and in a later section (*Chapter 3, CCA in wood*) the attempts to remove CCA from the wood by extraction is described in more detail, since this is the most relevant option in connection with the work presented in this thesis. The above mentioned reviews are recommended for more detailed information on the different disposal options.

The management options for CCA-treated wood include landfilling, reuse, either directly or recycled as components in other products and thermal treatments (incineration/combustion, pyrolysis or gasification).

#### 3.1. Landfill disposal

Landfill disposal is not a preferred permanent option for waste management of CCA-treated wood, because it does not recover any value from the product and it may be costly (*Cooper et al. 2001a*). In addition, landfill of organic wastes will not be allowed in the EU by 2005 (*Helsen & Van den Bulck 2004*).

In Denmark landfilling is currently the only waste option for CCA-treated wood.

### 3.2. Reuse and recycling

CCA-treated wood may be reused directly or recycled as smaller pieces in different composite materials. These products include cement-bonded particle boards (*Zhou & Kamdem 2002, Smith et al. 1994*), particle boards (*Munson & Kamden 1998*), fiberboards (*Felton & DeGroot 1996*) and flakeboards (*Gardner & Mengeloglu 1998*). A consumer survey by *Smith & Shiau (1998)* revealed that most of the responding wood composite manufacturers were not in favour of using CCA-treated waste wood in their production. The primary concerns were the safety of workers and environmental problems (*Smith & Shiau 1998*).

Even though reuse or recycling of CCA-treated waste wood reduces the need of new CCA-treated wood, it is not a solution of the waste problem, since the recycled wood eventually will end up as waste and need handling. When these mixed materials turns up as waste it may not be obvious that it contains CCA and incorrect handling (e.g. uncontrolled combustion) of the CCA-treated waste wood may occur.

In Denmark reuse of CCA-treated waste wood is generally not allowed. Dispensations may be given on individual basis for direct reuse of electricity poles but with the implementation of the EU directive reuse of CCA-treated wood is no longer allowed in marine environments (*BEK nr. 536 af 18/06/2003*).

### 3.3. Thermal treatments

Thermal breakdown of CCA-treated waste wood has the advantage of energy recovery plus the significant reduction of waste volume. Several researchers have studied the pyrolysis, gasification or combustion/incineration of CCA-treated wood. A general issue of concern is emission of As. Percentages of As volatilised have been reported to range from 8 to 95%, depending on the experimental conditions, and a threshold level (temperature and time) below which zero arsenic release is guaranteed, will be very difficult or even impossible to reach in large industrial installations without flue gas cleaning (*Helsen & Van den Bulck 2004*).

Meanwhile there is still a matter to cope with when methods to avoid As emission are implemented; the residues (ashes) with increased concentrations of Cu, Cr and As. These ashes may be landfilled after pre-treatment to avoid leaching of CCA, or the metals may be recovered and reused. In (*Ottosen et al., 2004*) two different residues after thermal treatment are characterized: a mixed bottom and fly ash from combustion of CCA impregnated wood and a charcoal from pyrolysis of treated waste wood. The two residues from the two different thermal processes were very different and a method for handling residues must be developed after the thermal treatment method, due to the high risk of leaching of Cu, Cr and As.

At Kommunekemi (an independent limited company, owned by the Danish municipalities) both gassification and pyrolysis has been tested for treatment of waste wood in pilot scale. However most of the results are confidential and at present the method is under evaluation at Miljøstyrelsen. The response from Miljøstyrelsen is awaited.

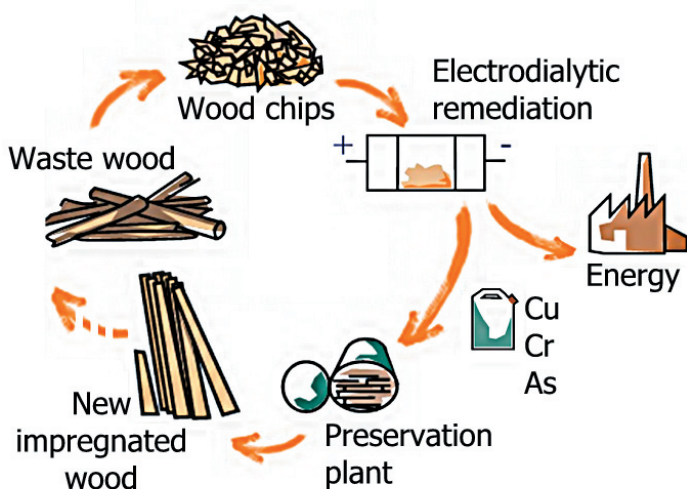
## 4. Electrodialytic remediation of CCA-treated wood

In the present thesis Electrodialytic remediation (EDR) is investigated as a possible alternative to the current disposal options. EDR uses a direct low voltage current as a cleaning agent and has the potential of recovering the removed Cu, Cr and As. The method is described in more detail in chapter 1 (Electrodialytic remediation)

In figure 2 a life cycle for CCA-treated wood is proposed; The wood is reduced to the size of wood chips before EDR. During EDR Cu, Cr and As are removed from the wood into liquids.

The remediated wood may be recycled in some form or incinerated, thereby utilizing the energy resource of the wood without the implications of As. In order to use the remediated wood as bio fuel, the removal of Cu, Cr and As has to be total. However in cases where As is removed and the concentrations of Cu and Cr are reduced, the wood may be burned in a municipal solid waste incinerator (MSWI).

The recovered Cu, Cr and As may be reused for the impregnation of new wood. Due to the recent restrictions of the use of CCA-treated wood in many countries, the metals may be reused for other purposes instead of new CCA preservative.



**Figure 2:** proposed life cycle for CCA-treated wood

The different parts of the life cycle will be addressed in the present thesis.

The structure of the thesis is seen below.

- The EDR principle is addressed in Chapter 1.
- In Chapter 2 the structure and impregnation of softwood is described. This chapter serves as a background for chapter 3.
- In Chapter 3 the CCA-wood interactions: fixation and distribution of CCA and the possibilities of extracting CCA from wood is described based on found literature.
- Chapter 4 is a presentation of the wood used in the experimental work
- In Chapter 5 the experimental conditions for the EDR experiments is described
- In Chapter 6 the EDR in laboratory scale is presented.

After Chapter 1-6 five papers are presented:

- Paper 1 presents the results obtained after scale up of the EDR process to pilot scale
- Paper 2 investigates the influence of metal pieces in the waste wood on the EDR process.
- In Paper 3 the possibility of reusing the removed Cu, Cr and As directly for impregnation of new wood is investigated.
- In Paper 4 the influence of EDR on the bending strength is investigated, to evaluate the possibility of reusing the wood instead of incineration
- Paper 5 investigates the distribution of CCA in partly remediated wood to evaluate possible limitations of EDR to remove specific CCA-wood interactions.

The main topic of this thesis was to investigate and optimize the EDR process to CCA-treated wood. The research is described in the above mentioned chapters and papers. During the process of optimizing and up-scaling the process, valuable information has been obtained that might be useful when other materials are considered for EDR. These observations and evaluations are described Chapter 7, the final chapter before the conclusions.

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# 1 EDR - Electrodialytic Remediation

The application of a low voltage direct current to soils for the removal of heavy metals or other pollutants is known as electrokinetic soil remediation. Worldwide 83 groups are currently working to improve the method, mostly for remediation of soil or harbour sediments. These groups are all members of a electrokinetic network that is managed at the Technical University of Denmark by Lisbeth Ottosen.

At DTU an advanced version of electrokinetic remediation is applied. It combines the principles of electrokinetic remediation technique with the use of ion exchange membranes to separate the electrode compartments from the soil and is known as Electrodialytic Remediation (EDR). The method was originally developed for removing heavy metals from polluted soil (*Ottosen 1995, Hansen 1995*).

## 1. Principle of EDR and remediation of soil

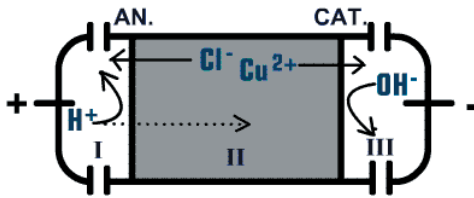
The main principle used in EDR is that ions (including heavy metal ions) move in an electric field:

When an electric field is applied to a water saturated soil matrix, the current is carried by ions in the soil pore water and moves according to their charge. Negative ions (anions) moves towards the positively charged electrode (anode) and positive ions (cations) moves toward the negatively charged electrode (cathode). This movement of ions in the electric field is called electromigration

In materials such as fine-grained soils, where there are charged particles (e.g. clay), balanced by mobile counter ions in an electric double layer, two other electrokinetic phenomena besides electromigration may also take place: electroosmosis and electrophoresis.

Electroosmosis is the flow of solution (water) relatively to a stationary solid phase (the soil matrix) and electrophoresis is movement of small charged particles (e.g. clay) relatively to the liquid phase. In the case of a negatively charged clay soil, the osmotic flow of water will be towards the cathode and the electrophoretic flow of clay particles will be in the direction of the anode. The electrokinetic phenomena in EDR is described in more detail in *Ottosen (1994)*.

The EDR cell is presented in principle in figure 1



**Figure 1:** Schematic presentation of the three-compartment EDR cell. (I) anode compartment, (II) middle compartment. (III) cathode compartment. CAT: cation exchange membrane. AN: anion exchange membrane.

The traditional EDR cell consists of three compartments: an anode compartment (I), a cathode compartment (III) and a middle compartment (II) where the soil is placed (figure 1). In the anode and cathode compartments (I & III) inert electrodes are placed and separate circulation systems for anolyte and catholyte solutions are used. Electrodes are placed in circulating solutions rather than directly in the soil to obtain an even distribution of current through the soil. At the same time it is possible to control the immediate surroundings of the electrodes, e.g. adjust pH during remediation. Electrode reactions (described later) may lead to formation of gas, that will be removed from the electrodes by the circulating electrolyte

The cathode compartment is separated from the middle compartment by a cation exchange membrane, a membrane that ideally only allows cations to pass. The anode compartment is separated from the middle compartment by an anion exchange membrane, which allows only anions to pass.

When an electric potential is applied to the electrodes, the current in the cell is carried by ions in the solutions in the compartments. Due to the placement of ion exchange membranes, there is a net transport of ions out of the soil, since ions may not pass from the electrode compartments into the soil in the middle compartment.

The selectivity of the ion exchange membranes allow ions to migrate from the middle compartment into the electrode compartments, but prevent ions from moving from the electrode compartments into the middle compartment. Thereby current is not wasted by carrying ions from one electrode compartment, through the soil and into the opposite electrode compartment. Also competition between these highly mobile ions from the electrode compartments and the ions in the middle compartment is avoided.

In this way the heavy metals (and other ions) are removed from the soil and into the electrode compartments from where they may be recovered by precipitation or electro deposition.

During remediation, reduction reactions will take place at the cathode and oxidation will take place at the anode. The nature of this electrode processes will depend on the electrode material, and the chemical species available in the electrolyte. In the case of



inert electrodes and low concentration of ions in the electrolyte the primary electrode reactions would be oxidation and reduction of water:

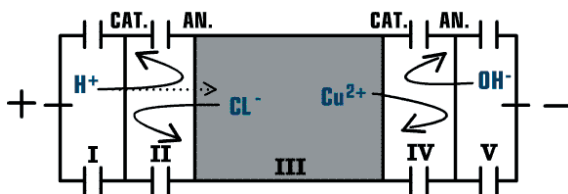
- (1) Anode:  $2\text{H}_2\text{O} \rightarrow \text{O}_2\uparrow + 4\text{H}^+ + 4\text{e}^-$
- (2) Cathode:  $4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{H}_2\uparrow + 4\text{OH}^-$

The oxidation of water at the anode (1) will result in increasing acidic conditions in the anolyte and the reduction of water at the cathode (2) will result in increasing alkaline conditions in the catholyte, unless pH is adjusted during the remediation. This is possible in the present system where electrodes are flushed during remediation.

In addition to the above mentioned reactions, redox reactions with ions present in the surrounding electrolytes can also take place. These reactions may include reduction of metals (e.g. Cu) at the cathode (3) and oxidation of chloride ( $\text{Cl}^-$ ) at the anode (4):

- (3) Cathode:  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
- (4) Anode:  $2\text{Cl}^- \rightarrow \text{Cl}_2\uparrow + 2\text{e}^-$

Reaction (3) will lead to Cu precipitated on the electrode and reaction (4) will lead to the formation of gaseous chloride. Since gaseous chloride is poisonous and increasing amounts of metal precipitations on the electrodes may interrupt the electric field, it may be beneficial to avoid these electrode reactions. This can be done by introducing two additional compartments (II & IV) to the set-up as shown in figure 2.



**Figure 2:** Schematic presentation of the five-compartment EDR cell. (I) anode compartments, (II) & (IV) collecting compartments, (III) middle compartment, (V) cathode compartment. CAT: cation exchange membrane. AN: anion exchange membrane.

The collecting compartments (II & IV) are placed between the electrode compartments and the middle compartment, and by a system of ion exchange membranes, the ions which are removed from the middle compartment are trapped due to the outer pair of membranes and concentrated in these compartments and will not reach the electrodes.

During EDR of soil an acidic front is often seen to emerge from the anode side of the soil. The acidification is caused partly by water splitting at the anion exchange membrane (*Ottosen et al. 2000*) and partly by protons passing from the anolyte into

the middle compartment since anion exchange membranes may not be able to retain protons.

In most cases the acidic front is desirable since it may enhance the solubility of the heavy metals that may be precipitated or adsorbed to the soil particles.

Removal of heavy metals from soil by EDR has been studied intensively in the last decade and several articles have been published on the subject. EDR often needs to be optimised for each soil individually and the optimisation of the process is ongoing. EDR principle has also been transferred to other waste materials polluted with heavy metals.

## 2. EDR of other waste fractions

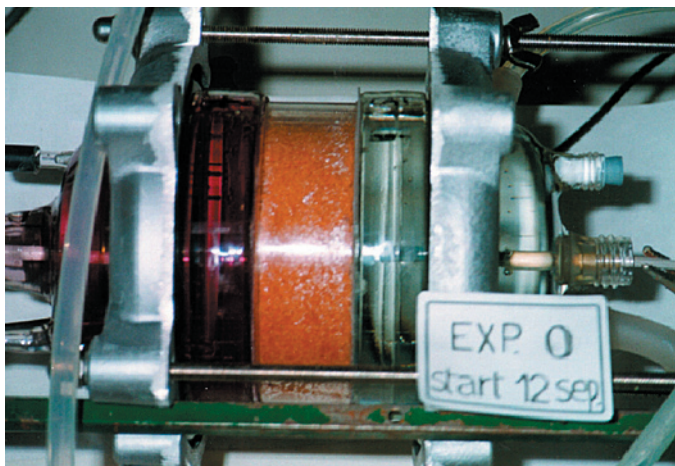
Heavy metals have been removed from different types of fly ash (*e.g. Hansen 1998, Pedersen 2002*) and an up scale of the removal of cadmium from biomass combustion ash (*Pedersen et al. 2004*) is now under consideration.

Removal of heavy metals from harbour sediments by EDR is the topic of an ongoing Ph.D. thesis and the results obtained so far has been very good (*Nystroem et al. 2004*). Cadmium has been removed from waste water sludge by EDR (*Jakobsen et al. 2004*) with promising results.

In the remediation of fine-grained materials like fly ash and harbour sediments, the use of a stirred system has proven beneficial. Instead of the traditional EDR setup where the material is merely water saturated before it is placed in the middle compartment, an ash- or sediment-slurry is placed in the middle compartment and continuously stirred during the EDR experiment. This has significantly improved the EDR of both fly ash and harbour sediments (*Pedersen 2002, Nystroem et al. 2004*). The stirred system has also been applied to a fine fraction of soil ( $< 125 \mu\text{m}$ ) and here it proved to increase the removal rate of the heavy metals while the duration of the experiments and the charge consumption was reduced.

### EDR of CCA-treated wood

The first EDR experiments on CCA-treated wood were made by Dr. Ribeiro (2000). The experimental setup was similar to the one used for soil remediation (figure 1). Sawdust ( $< 0.84 \text{ mm}$ ) prepared from an out of service pole was used in the experiments. Prior to the remediation the sawdust was saturated with oxalic acid and packed to a uniform mass in the middle compartment, see figure 3. The middle compartment was 3 cm long and 75 g sawdust was used. Good results were obtained with oxalic acid as an additive. At the end of a 30 days experiment 93% Cu, 95% Cr and more than 99% As was removed from the wood. In a similar experiment with water instead of oxalic acid, 91% Cu, 27% As and negligible amounts of Cr was removed.

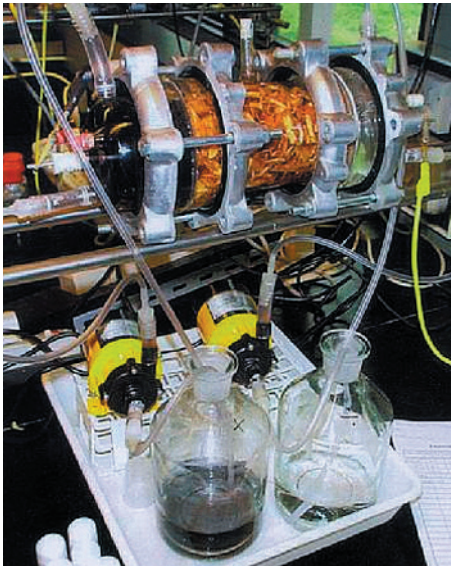


**Figure 3:** Electrodealytic remediation of sawdust. (*Ribeiro et al. 1999*).

Left side: Anode, right side: Cathode.

The experimental work presented in this thesis is based on the pioneer work by Dr. Ribeiro. However it was decided to use wood chips instead of sawdust, to investigate the possibility of removing CCA from larger size fractions. By using chips instead of sawdust, less processing of the treated wood is required. Thereby the workers will be exposed to airborne particles to a lower degree, and a safer work environment will be created.

When wood chips are placed in a middle compartment of a EDR cell, there is some free space, since wood chips can not be packed as neatly in the middle compartment as sawdust. The free space has to be filled by the liquid phase in order to ensure even distribution of the current. This leads to higher L:S (liquid to solid) ratios in the remediation of wood chips, compared to sawdust. When wood chips was used, the L:S ratio was approximately 6, while a L:S ratio close to 3 was used in the remediation of sawdust.



**Figure 4:** Electrodealytic remediation of wood chips. Left side: Anode, right side: Cathode.

The same EDR set-up was used both for sawdust and chips and figure 4 shows an EDR experiment with wood chips.

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## 2 The composition and impregnation of softwood

The objective of this chapter is to present the composition of wood and the methods that are used for impregnation of wood commercially.

Wood may be divided into two categories: Hardwood (Angiosperms, deciduous trees) and softwood (Gymnosperms, conifers). Hardwood includes trees like oak and beech, while softwood includes pine and spruce.

The structure of the hardwood is more varied and complicated than softwood but most structural concepts are similar in the two wood types.

Here only softwood will be described since this is the wood type of most importance when commercial wood preservation is considered. Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) are the species most used for wood preservation in the Denmark, and the difference in structure of pine and spruce are outlined when encountered.

### 1. Structure of softwood

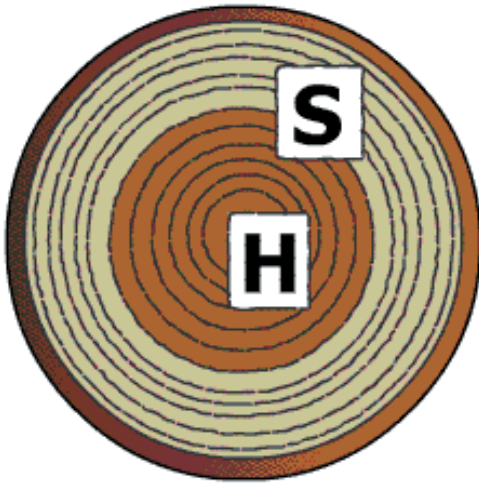
Softwood shows a relatively simple structure. It consists of tracheids, rays and resin canals (*Sjöström 1993*). The large cavities (lumen) inside the tracheids and rays makes the average density of softwood in the range of 0.35 -0.55 g/cm<sup>3</sup> (oven-dry mass to green volume)(*Rowell 1984*). The fibre saturation point (FSP), defined as the moisture content when cell walls is saturated with moisture but no free water exists in the lumen, is between 25% and 35% for most species. In air dried wood the equilibrium water content is approximately 12% (at 65% relative humidity, 20°C) (*Hoffmeyer 1995*).

#### 1.1. Heartwood and Sapwood

A cross section of a tree trunk is illustrated in figure 1. The outer, lighter part of the log is known as the sap wood and conducts the upward flow of sap from the roots. The central darker part of the log is the heart wood and consists only of dead cells. The proportion of heartwood becomes larger as the tree grows and the formation of heart wood is associated with the wood drying out and becoming infiltrated with deposits of resins and aromatic compounds. These deposits reduce the porosity of the cells and are often significantly toxic, so that heartwood is usually more resistant to attacks by fungi or insects compared to sapwood (*Thomas 1981*). Not all wood species form discoloured heartwood, so recognition of heartwood based on colour is not always possible. In Norway spruce for example it is not possible to distinguish between sapwood and heartwood by colour (*Thomas 1981*).

For the purpose of wood preservation, sapwood is preferred, since the heartwood of e.g. Scots pine is virtually impermeable (*Hoffmeyer 1995*). In addition heartwood is

often more durable than sapwood due to the reduced porosity and toxic deposits as mentioned above.



**Figure 1:** Cross section of a tree trunk.  
S: sapwood, H: Heartwood.

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## 1.2. Growth rings

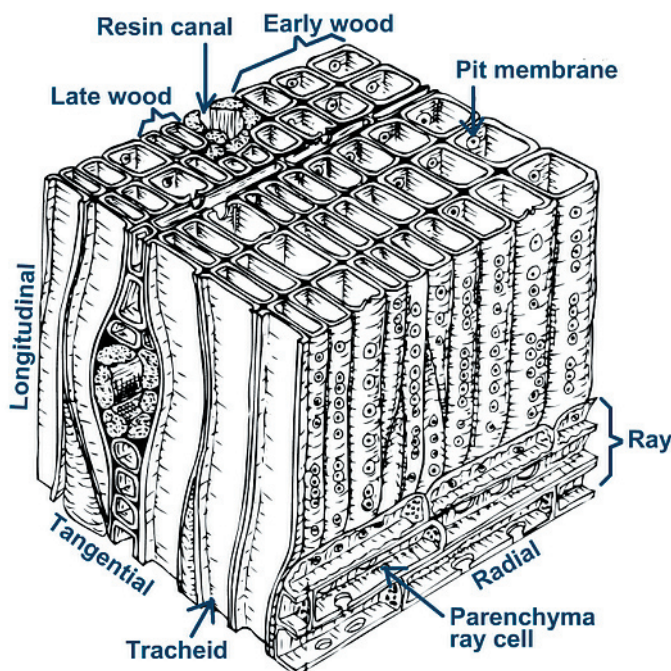
The fine dark rings that can be seen in the cross section in figure 1 are growth rings and shows the latewood fraction of the wood. The lighter part between two growth rings is early wood. Early wood is the wood formed in spring and they are large thin walled cells. As spring turns into summer the cell walls get thicker and the cells are smaller. This leads to the fact that latewood has a higher density compared to early wood (*Thomas 1981*).

## 1.3. Cells in softwood

Softwood is mainly composed of tracheids (90-95%) and ray cells (5-10%). Resin canals are also found in softwood but accounts for only 0.1-1% of the wood (*Sjöström 1993*).

In figure 2 the orientation of the different cell types are shown in a schematic presentation of a cube of softwood.





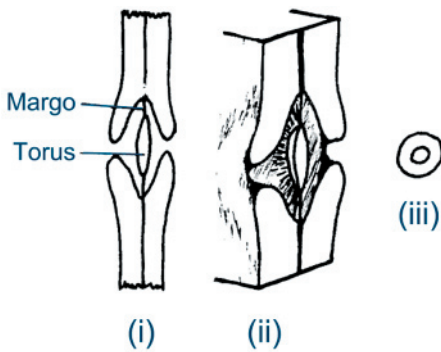
**Figure 2:** Schematic presentation of softwood structure. Adapted from Thomasson (1995)

## Tracheids

Tracheid cells, often referred to simply as wood fibres, are long and slender (2-5 mm long and 10-50µm wide) with flattened or tapered closed ends (*Hoffmeyer 1995*). They are oriented in the longitude direction and gives softwood the mechanical strength required. Tracheids also provide for water transport in the sapwood, which occurs through the thin-walled early wood tracheids with their large cavities. The tracheids make up most of the wood substance as it accounts for 90-95%.

The tracheids are connected by bordered pits that are placed on the radial surfaces of the tracheids (*Rowell 1984*). Two complimentary pits normally occur in neighbouring cells and thereby a pit pair is formed, see figure 3. The liquid transport from one tracheid to another takes place through the bordered pits. The centre of the membrane is a thickened cellulose disc structure called torus. The margo is a net-like membrane that connects the torus to the cell walls. The margo is also composed of cellulose in the form of microfibril strands and here liquid can pass between to adjacent tracheids. During drying of the wood the torus is pulled to one side and the pit closes. Bordered pits in this position are described as aspirated and in certain softwood species, like spruce where aspirated pits are common in dried timber, the wood is particular difficult to treat with preservative solution (*Eaton & Hale 1993*).



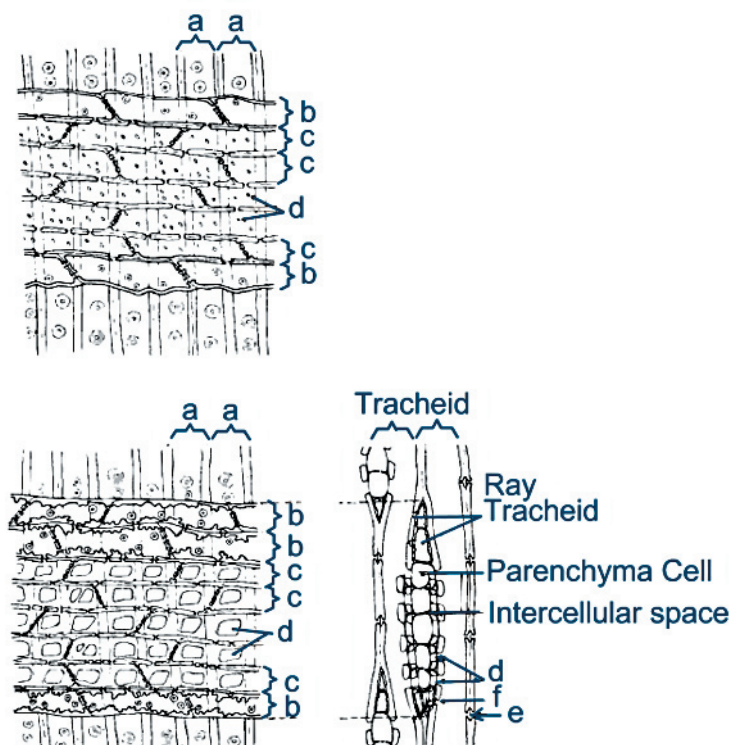


**Figure 3:** Boarded pit membrane. (i) side view, (ii) 3D view, (iii) front view. (*Eaton & Hale (1993)*).

## Rays

Rays are narrow ribbons of cells that are oriented in the radial direction, perpendicular to the tracheids. See figure 2. The width of a ray (tangential direction) usually corresponds to one cell. The height is made up of several cell layers (*Sjöström 1993*). Several parenchyma ray cell rows are stacked on top of each other and are often placed between a single or double row of ray tracheid cells. In figure 4 the structure of rays (pine and spruce) are shown in a schematic sketch. Parenchyma cells are small thin walled bricklike cells (*Thomas 1981*). They differ from the tracheids by remaining alive for some years after their development is completed (*Sjöström 1993*). Ray tracheids may be similar in size to parenchyma cells but often have thick sculptured cell walls. Ray cells are connected to the perpendicular oriented tracheids by cross field pits. In ray tracheids the pits are bordered (see figure 3) but the ray parenchyma cells are connected to the tracheids (longitude) by simple or nearly simple pits (*Desch 1968*). The cross field pits in spruce and pine are quite different, as can be seen in figure 4. In pine the pits are large and window-like whereas the pits in spruce are much smaller with an elliptic form.

Ray parenchyma cells has also a major role as a storage holder and frequently contain materials such as fats, starch and various sugars (*Rowell 1984*).



**Figure 4:** Radial section of a spruce ray (above) and radial and tangential section of a pine ray (below). (a) Longitudinal tracheids. (b) Rows of ray tracheids (small bordered pits). (c) Rows of ray parenchyma. (d) Pits in the cross fields leading from ray parenchyma to longitudinal tracheids. (e) A bordered pit pair between two tracheids. (f) A bordered pit pair between a longitudinal and a ray tracheid (Sjöström 1993)

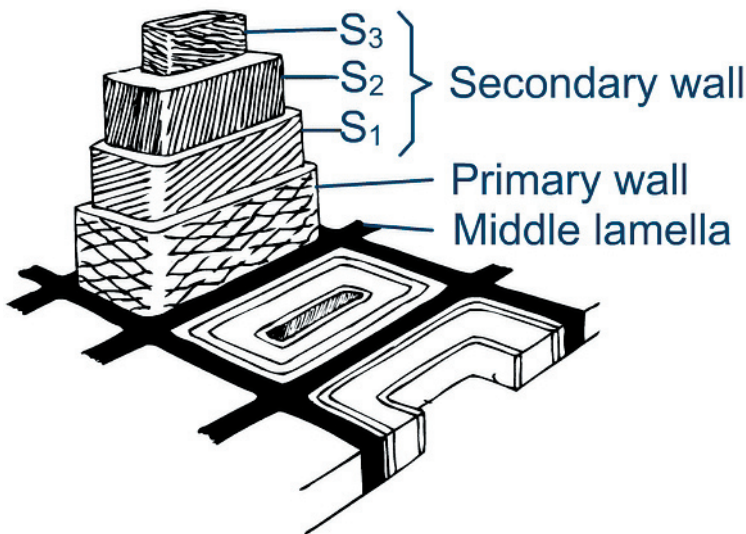
## Resin canals

Resin canals, also called resin ducts are tube like voids that may be oriented both longitudinally and radially throughout the wood (see figure 2). Horizontal canals are always located inside the rays. A layer of epithelial cells (parenchyma cells) surrounds the resin ducts and secrete resin into the canals. In pine wood the resin canals are most abundant and larger than in spruce. In pine wood the resin canals are concentrated in the heartwood whereas in spruce they are evenly distributed throughout the wood.

## 2. Cell structure of wood fibres

The major constituents of wood are cellulose (40-55%), hemicelluloses (20-30%) and lignin (18-33%) and the three components are found in different places in the wood cell (*Eaton & Hale 1993*). In figure 5 the structure of a wood cell is presented. The middle lamella consists mainly of lignin and is located between the cells with

the purpose of binding them together. A wood fibre cell are composed of a primary and a secondary wall. The Primary wall is a thin layer and consists of cellulose and hemicelluloses and completely embedded in lignin. The secondary wall consists of three layers; S1, S2 and S3 built up by bundles of microfibrils that is highly ordered groupings of cellulose that is embedded in a matrix of hemicelluloses and surrounded by lignin. The three secondary wall layers differ in the orientation of microfibrils and thickness of layer. The S2 layer is considerably thicker than the S1 and S3 layer and the microfibrils in the S2 layer are almost align with the longitude direction of the wood (*Eaton & Hale 1993*). These two factors makes the S2 layer a significantly contributor to the high strength properties of wood parallel to grain (*Thomas 1981*).



**Figure 5:** A telescoped view of wood cell layers showing the orientation of cellulose microfibrils in each layer. (*Eaton & Hale 1993*)

### 3. Impregnation of softwood

In connection with impregnation of wood the sapwood is of most interest, since the characteristics that make heartwood decay-resistance: very slow to absorb moisture and denser than sapwood, also makes it difficult to treat with preservatives (*Eaton & Hale 1993*). Two different methods are used commercially when pine and spruce are to be impregnated: pressure treatment and sap displacement.

#### 3.1. Impregnation by pressure treatment

In conventional pressure treatment methods the preservative solution is forced into the wood as a result of high pressure (7-14 atm.) being applied to the wood (*Richardson 1993*). The methods may be divided into full-cell and empty-cell methods.

In full-cell impregnation a vacuum is introduced prior to the pressure to remove the air from the wood cells and thereby facilitate the penetration of the preservative. The Bethell method is a full-cell method with vacuum both before and after the pressure treatment (*Richardson 1993*).

In empty cell impregnation no initial vacuum is used. Thereby air is still present in the wood cells when the preservative solution is introduced under pressure. After the pressure is released the air that was trapped within the wood will expand and eject the preservative solution from the porous spaces in the wood. In practise a vacuum is often drawn during this stage to encourage the expansion of the trapped air. The Lowry method is an example of an empty-cell method (*Richardson 1993*).

When pine is impregnated by pressure treatment methods, full penetration of the sapwood can be obtained. In spruce the penetration is 0-6 mm (*Nyborg 2004*)

### 3.2. Impregnation by sap displacement

Sap displacement can be used for impregnation of poles and here the preservative solution is introduced to the green wood. After placing the pole in the preservative solution, vacuum is applied to either one or both ends of the pole to remove the sap while preservative solution is induced simultaneously. The Gewecke (or Saug-Kappe process) is a sap displacement method where a conical cap is fitted on the top end of the pole, while the bottom end is placed in a preservative reservoir. When vacuum is applied, the preservative solution is absorbed from the bottom end, while sap is being removed from the top end.

### 3.3. Differences in impregnation of pine and spruce

The difference in wood preservative penetration in pine and spruce may be attributed to the differences in structure of the wood in the two species.

In pressure treatment methods both tracheids and rays play an important role as the preservative solution may penetrate into the wood radial through the rays and longitudinal through the tracheids.

The fact that pine has large window pits in the cross field between rays and tracheids as opposed to the much smaller pits in spruce (*see figure 4*) presumably makes penetration of preservative through rays more difficult in spruce. In addition to that pit aspiration is often associated with spruce. In pressure treatment dry wood is used and when spruce dry, the tracheids close and pit aspiration occurs. The low penetration of the preservative solution during pressure treatment is due to the pit aspiration in spruce (*Richardson 1993*).

Spruce poles may be impregnated by sap displacement. Here the preservative solution is introduced to the green wood to avoid pit aspiration and the sap is removed by vacuum and simultaneously replaced with the wood preservative solution (*Richardson 1993*).

## 4. Summarising conclusions

The structure of softwood is fairly simple and consists mainly of tracheids (90-95%) and rays (5-10%). Most of the wood is dead material and only parenchyma cells are alive for some years after the cells are developed. In the ray parenchyma cells materials such as starch and sugars may be stored.

In impregnation of wood mainly sapwood is considered due to the impermeable structure of heartwood. The pressure impregnation method is most suited for impregnation of pine where it provides full penetration of the sapwood. In spruce the penetration is only 0-6 mm due to the smaller cross section pits and bordered pit aspiration of spruce.

Spruce poles may be impregnated by sap displacement methods where the sap is removed from the green wood by vacuum and simultaneously replaced by the preservative solution.

In industrial scale wood preservation of long pieces of timber, the preservative solutions may penetrate into the wood both from the side, through the rays and from the end of the wood, through the tracheids.

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# 3 CCA in wood:

## Fixation, distribution and extraction

In this chapter the wood preservative CCA (Chromated Copper Arsenate) is presented, followed by a description of different theories found in the literature on the fixation of CCA in wood following impregnation. Findings from the literature on the actual distribution of CCA in the wood after impregnation are presented afterwards and finally different attempts to extract the CCA components: copper (Cu) chromium (Cr) and arsenic (As) from wood will be introduced.

The study is limited to the description of CCA since this is the preservative of the out most importance. It has been banned for use in Denmark for more than 10 years, but as a waterborne preservative it was used extensively until it was banned due to the presence of As (*Hansen et al. 1997*) Since the average service life of CCA treated wood may be 30 years or more, the waste wood that is present now and in years to come, will still be dominated by CCA.

The replacements for CCA included CC (copper, chromium) formulation and Cu and boron (B) formulations. The fixation of CC formulations is probably similar to the fixation of Cu and Cr in CCA formulations, whereas the fixation of B and the fixation of Cu in preservative formulations without Cr must rely on other mechanisms.

## 1. CCA formulations

The first CCA formulation was called Ascu, after the As and Cu present in it and was patented in 1933 by Kamesan from India. The formulation was in the form of arsenic pentoxide ( $\text{As}_2\text{O}_5$ ,  $2\text{H}_2\text{O}$ ), copper sulphate ( $\text{CuSO}_4$ ,  $5\text{H}_2\text{O}$ ) and potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ). The molar ratio of Ascu was 1:1.6:2.3 (As:Cu:Cr) (*Eaton & Hale 1993*). In Sweden a similar CCA formulation, based on metal oxide was developed. This formulation was called Boliden K33 and was first introduced in 1949 (*Richardson, 1993*). Several CCA formulations has been developed since, with the content of Cu, Cr and As in common, but with different mole ratios.

The different CCA formulations has since been categorised into three different types based on the ratio of the three components. AWPA (American Wood-Preservers Association) defines types A, B and C based on the relative amount of active oxides, but they also applies to salt containing CCA formulations. The relative amount of active oxides may be converted into mole ratios as presented in table 1. The molar ratios in table 1 are mean values, but the relative amount of oxides as given by AWPA are intervals.

**Table 1:** Average Cr:Cu:As Mole ratios in CCA formulations (adapted from *Richardson, 1993*)

	CCA-A	CCA-B	CCA-C
Cr	4.6	0.9	1.6
Cu	1.6	0.6	0.8
As	1	1	1

CCA-A is a formulation that is high in Cr and low in As, and CCA-B is high in As and low in Cr, but in the 1960s the debate was centred on the optimum balance to achieve best fixation of CCA (*Connell 1991*). This led to the CCA-C formulation that is by far the most used formulation today because it is considered to have the best leach resistance and field efficacy of the three formulations (*Forest Products Laboratory 1999*). In the Nordic countries, the shift from CCA-B to CCA-C took place in 1985-1986 (*Nyborg 2004*). The shift was however not instant. In Sweden CCA-B was still used in 1993 (*Jermer & Nilsson 1999*).

## 1.1. Retention levels of CCA

The requirement to the retention level (loading) of CCA in the wood after impregnation depends on the environment the wood is intended for. In general a low retention level is required for wood to be used above ground and higher retention levels are required for wood in ground contact and in contact with seawater. The retention levels are given in mass CCA per volume of sapwood. However there are two different standards available. In the Nordic countries a set of retention levels are outlined by the Nordic Wood Preservation Council (NWPC or NTR). The loading is given in mass of the actual CCA formulation (regardless of oxide or salt formulations) per volume of sapwood. The retention levels range from 5 kg/m<sup>3</sup> to 24 kg/m<sup>3</sup> (*NTR, 1999*). AWPAs recommend retention levels of 4-40 kg/m<sup>3</sup> (*AWPA, 1996*) but this is kg CCA as oxide per m<sup>3</sup>. For wood in ground contact the recommended retention level of CCA is 12 kg/m<sup>3</sup> according to NTR and approximately 9.6 kg/m<sup>3</sup> according to AWPAs.

## 1.2. CCA as a wood preservative

CCA preservatives are accepted as some of the most effective treatments for the protection of wood against fungi, insects and marine borers. (*Eaton & Hale 1993*)

Cu is recognized as a fungicide by precipitation of proteins within the fungi and by interfering with enzyme reactions.

As is an effective insecticide and also serves as a fungicide to copper tolerant fungi. (*Anderson et al. 1991*)

Generally Cr is not recognized for its role as a pesticide but in CCA it serves a very important purpose, as it is responsible for the strong fixation of Cu and As in the wood.



## 2. Fixation of CCA in wood

The fixation of CCA in wood may not be fully understood, but several articles have been published on the subject. In the following the fixation of CCA in wood is illustrated by the authors: *Dahlgren & Hartford (1972-1975)*, *Pizzi (1981-1983)* and *Bull (2001)*. Main focus will be on the final fixation products in the wood and less details will be given on the process and intermediate compounds that are formed during the fixation process.

### 2.1 Fixation described by Dahlgren & Hartford

In 1972-1975 Dahlgren (& Hartford) published a series of articles concerning the fixation of CCA to wood. (*Dahlgren 1975, 1974, 1972, Dahlgren & Hartford 1972a, 1972b, 1972c*) The preservation of pine and spruce (and in one occasion larch) were investigated and both salt free (oxides) and salt containing (Na, K, SO<sub>4</sub>) CCA formulation were used.

The experiments were mainly performed on sawdust, although some conclusions e.g. concerning the reduction of hexavalent chrome (Cr (VI)) were based on studies of solutions in the absence of wood (*Dahlgren & Hartford 1972b*)

In the investigations by Dahlgren and Hartford sawdust and preservative solution is mixed and the fixation process is monitored by pH measurements and analyzes of the liquids and formed precipitates. Dahlgren (1972) emphasis that wood must be incorporated as an essential part of the reaction system to give a picture of what actually happens, even if this makes evaluation considerably more complicated. Dahlgren & Hartford admits to the use of available chemical knowledge, indirect evidence and hypotheses to some extend (*Dahlgren 1972*).

Dahlgren suggests that the CCA-wood interaction can be divided into three periods: An initial instant reaction followed by a primary precipitation fixation period divided into 4 regions by different Cr reduction rates, and finally a final reaction or conversion period. The length (or presence) of all four regions in the main precipitation fixation period depends on the wood species, solution strength and CCA formulation. (*Dahlgren 1975*)

The initial instant reaction is characterised by a sudden extensive increase in pH. This is explained primarily by adsorption of chromic acid to the wood, most likely to the cellulose (*Dahlgren & Hartford 1972a*). During the main fixation period, the pH reaches a maximum, when all Cr is precipitated, followed by a slow final reaction or conversion period with alternating decrease and increase of pH until it reaches its final value. (*Dahlgren & Hartford 1972c*) In the experiments by Dahlgren & Hartford, the final pH seemed to be reached after approximately 3-6 months (*Dahlgren & Hartford 1972a*). In spruce the final pH was 4.9-5.7 depending on the CCA formulation and in pine the final pH was between pH 4.0 and pH 5.3. The lowest pH was found after impregnation with 2.0 % Boliden K33 and the highest pH was due to impregnation with 2.5

% Tanalith C (*Dahlgren & Hartford 1972a*). Boliden K33 is a salt free formulation and Tanalith C is a salt containing formulation.

Some of the compounds formed during the main precipitation fixation period are not stable and conversion into stable compounds takes place via dissolution in the final conversion period (*Dahlgren 1972*)

One of the intermediates suggested is a complex containing both Cr(III) and Cr(VI). The suggestion is based on pH measurements and the assumption that Cr(III) is needed in order to fixate Cr(VI) (*Dahlgren & Hartford 1972b*). This complex is presumed to be converted into Cr(III) during the conversion period (*Dahlgren 1974*):

(i)  $2[\text{Cr}(\text{CrO}_4)_3^{3-}](\text{to the wood}) + 6\text{H}^+ + 9\text{H}_2\text{O} \rightarrow 8 \text{Cr}(\text{OH})_3 + 9\text{O}$  (oxygen for wood oxidation)

## Fixation products according to Dahlgren & Hartford

According to Dahlgren and Hartford (*1972c*) the final equilibrium fixation products are:

- ▶ ion-exchange fixation of Cu to the wood
- ▶  $\text{CrAsO}_4$
- ▶  $\text{Cu}(\text{OH})\text{CuAsO}_4$
- ▶  $\text{Cr}(\text{OH})_3$

In freshly treated wood fixed hexavalent chrome occurs, but it disappears on storage at ordinary temperatures after some months. As these instable compounds have a low solubility and thus a slow dissolution rate, the final conversion reactions of e.g. chromic chromates ( $\text{Cr}(\text{CrO}_4)_3^{3-}$ ) are very slow. (*Dahlgren & Hartford 1972c*)

## 2.2. Fixation described by Pizzi

In the 1981-1983 Pizzi published a series of articles on the chemistry and kinetic behaviour of CCA wood preservatives. (*Pizzi 1981, 1982a, 1982b, 1982c, 1983*).

In addition to experiments with different CCA compositions, Pizzi also presents experiments with only chromium trioxide ( $\text{CrO}_3$ ), a Cr/As system and a Cr/Cu system. The experiments were performed on cellulose, lignin and their model compounds (D(+)-glucose and guaiacyl units) as well as milled pine wood flour.

The fixation process was monitored by measurement of pH as well as element and atomic adsorption analyses of formed precipitates. The Cr(III) formation (by reduction of Cr(VI)) was monitored by UV/visible Spectrophotometry analyses at 595 nm. Spectrophotometry was also used for analysing remaining metals in the solutions after precipitations.

The fixation process suggested by Pizzi consists of an initial instant reaction followed by the main precipitation and fixation period that may be divided into three reaction zones. The initial instant reactions include ion exchange fixation of Cu and a tem-

porary ion exchange take up of protons and adsorption of chromic acid onto wood (Pizzi 1981). The three reaction zones in the main precipitation and fixation period differs in reaction rates of the Cr(VI) reduction (Pizzi 1981). In the first zone Cr(VI) is absorbed on cellulose and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) form complexes with lignin units. In the second zone chromate ( $\text{HCrO}_4^-$ ) reacts with lignin to form complexes and the third zone consists mainly on reduction of Cr(VI) to Cr(III) on cellulose sites (Pizzi 1982a). The presence or length of the second reaction zone depends highly on the composition of the CCA, especially on the Cr:As ratio (Pizzi 1982b). As is proposed to be fixed as Cr(III)arsenate ( $\text{CrAsO}_4$ ). Increasing the amount of As, means higher amounts of Cr(III) arsenate formed during the second reaction zone, and thereby the lower the amount of Cr(VI) available for reaction as  $\text{HCrO}_4^-$  with lignin in the second reaction zone. (Pizzi 1982c). The duration of the experiments by Pizzi is limited to 6 hours and Pizzi expects no presence of a conversion period as suggested by Dahlgren and Hartford (Pizzi 1982c).

## Fixation products according to Pizzi

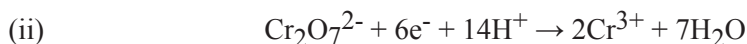
The final equilibrium fixation products according to Pizzi (1982c) are:

- Ion exchange fixation of Cu to wood (lignin and cellulose)
- $\text{CuCrO}_4$  – lignin complexes
- $\text{CrAsO}_4$  – lignin complexes
- $\text{CrAsO}_4$  precipitated onto cellulose
- $\text{CrO}_4^{2-}$ -lignin complexes

Pizzi also estimates the distribution of Cu and conclude that the majority of Cu (80-90%) is fixed to wood independently of Cr and As, most likely as ion exchange fixated Cu, but in the case of a salt containing CCA formulation with the presence of sulphate, a fraction of the Cu (5-20%) may be found as  $\text{CuSO}_4$  in the wood after fixation (Pizzi 1982c).

## 2.3. Fixation described by Bull

In a more recent study by Bull (2001) a fixation model is proposed and supported by a X-ray absorption fine structure spectroscopy (XAFS) analysis. The approach of Bull is simple and mainly based on the reaction of chromate with wood:



The reaction (ii) is proton consuming and will lead to an increase of pH in the wood. The increase of pH will in turn lead to precipitation of  $\text{CrAsO}_4$ , since it rapidly polymerises at a critical pH of 2.3 or less (Bull 2001). EXAFS (Extended X-ray absorption fine structure spectroscopy) analyses of treated wood indicated that As is predominantly bound to Cr, while Cu is not closely associated with any other heavy element (Bull et al. 2000). Cr may also precipitate as  $\text{CrO}_3$ . According to Bull (2001) chromates can be eliminated because Cr(VI) is definitely not present in fully fixed timber. In addition to inorganic fixation products, the metals may also be fixed onto binding

sites in the wood. Bull suggests that Cr(VI) is being reduced to Cr(III) while primary alcohol groups in the wood are oxidised to carboxylic acids. The fixation to the wood components are presumed to be dominated by Cu, since Cr(III) will precipitate as hydroxide relatively rapid at the low acidity conditions in the wood and As has precipitated as  $\text{CrAsO}_4$ . Primary alcohols are plentiful in both lignin and cellulose but Bull (2001) does not find the concept of distribution to be useful and therefore does not distinguish between the two wood components.

## Fixation products according to Bull

According to Bull (2001) the fixation products of CCA is dominated by:

- $\text{CrAsO}_4$
- $\text{Cr(OH)}_3$
- Cu – wood carboxylate complexes

In addition to the above mentioned, Bull (2001) does not rule out the occurrence of Cr(III) –wood carboxylate complexes but finds that chromium hydroxide ( $\text{Cr(OH)}_3$ ) is a much more plausible form. Copper arsenate ( $\text{Cu(OH)CuAsO}_4$ ) as proposed by Dahlgren & Hartford may also be present but not in any significant amount, according to the EXAFS analyses. (Bull *et al.* 2000)

## 2.4. Comparison of fixation theories.

When comparing the fixation theories of Dahlgren & Hartford, Pizzi and Bull, there are several shared findings/theories but also some disagreements. In the following the three fixation theories are compared.

There is an agreement on the fact that the reduction of Cr(VI) to Cr(III) is the driving force of CCA fixation in wood. There is also an agreement that this is a proton consuming process, and that the pH will increase during the fixation. During the reduction of Cr(VI) to Cr(III) sites in the wood will be oxidised and strong fixation sites for Cu and  $\text{CrAsO}_4$  may be created.

One of the main disagreements in the fixation theories presented here, is whether or not Cr(VI) is present in fixed wood.

### Presence of Cr(VI)

According to Dahlgren & Hartford Cr(VI) may be present in freshly treated wood, but is converted into stable Cr(III) compounds during storage (Dahlgren & Hartford 1972c). The conversion reactions are slow, due to low solubility and thus slow dissolution rate of the chromates.

Pizzi states that Cr(VI) indeed will persist after the CCA is fully fixed in the wood. In the theory by Pizzi, part of the Cr will be present as chromates ( $\text{CrO}_4^{2-}$ ) that is totally and irreversibly fixed to the wood and cannot leach (Pizzi 1982c). Pizzi does not believe a conversion period is taking place after the main fixation period.

In the system by Dahlgren & Hartford the experiments took place in a homogenous

system without water evaporation and the duration was up to 6 months (*Dahlgren & Hartford 1982a*). The duration of Pizzi's experiments were less than 6 hours and the finding that there is no conversion period are based on an experiment where the precipitate that was obtained after fixation was first left in the mother liquid, and then dried for 5 months (*Pizzi 1982c*). After the 5 months drying, Pizzi found no modification in the composition of the precipitate and concluded that no conversion period takes place. Bull (*2001*) states that no Cr(VI) is present in fully fixed wood but offers no evidence for this view other than this is generally demonstrated by chromotropic acid spot test. In addition to that, he refers to the work of Kaldas & Cooper (*1993*) that showed complete conversion to Cr(III). They used XPS (X-Ray photoelectron spectroscopy) and found that complete conversion to Cr(III) was obtained at elevated temperatures.

Dahlgren and Hartford states that a liquid phase is necessary in order for the final reactions to take place (*Dahlgren & Hartford 1972c*). This may be the reason for the different findings of Dahlgren & Hartford and Pizzi. If the liquid phase is maintained in the system of Dahlgren and Hartford, and not by Pizzi, the conversion from Cr(VI) to Cr(III) may take place in the first system, but not in the other.

In general the presence of a liquid phase may control the rate of conversion to Cr(III). If the fixation period is short and the wood is afterward left to dry/fixate, the wood may dry out before the conversion of Cr(VI) is complete, but if the wood is used in an outdoor environment, as CCA treated wood normally is, the wood may be moisturised during use and the conversion may take place. In elevated fixation temperatures (*Kaldas & Cooper 1993*) the conversion may take place faster due to the higher temperature and the fact that increasing the temperature often increases the reaction rate of chemical reactions.

If this is the case, then the findings of all the above authors may be explained.

## Fixation of Cu

Dahlgren & Hartford, Pizzi and Bull all agree that at least part of the Cu is fixed directly to the wood, independent of Cr and As. Pizzi and Bull states that almost all Cu may be fixed in this manner. Dahlgren & Hartford postulates that a significant part of Cu may also be fixed as copper arsenate ( $\text{Cu}(\text{OH})\text{CuAsO}_4$ ), and Bull agrees to the presence, although the amount seems insignificant when XAFS is applied. The reason for the difference may be due to different CCA formulations. Dahlgren uses CCA-B, where the Cr:As may be less than 1 (*see table 1*). This means that As may be fixed as both chromium arsenate (*see fixation of As*) and copper arsenate. Bull on the other hand investigates wood treated with type II (similar to CCA-C) and here the Cr:As ratio is typically 2. In this system there will be plenty Cr to fix all the As and therefore only small amounts of copper arsenate may be expected. Pizzi states that a small fraction of Cu is found to be copper chromate wood complexes ( $\text{CuCrO}_4$ ). This is not verified by either Bull or the findings of Dahlgren & Hartford, probably due to the proposed presence of Cr(VI).

## Fixation of As

Dahlgren & Hartford, Pizzi and Bull all agree that As is predominately bound to Cr. Chromium arsenate ( $\text{CrAsO}_4$ ) is proposed by all the above authors as the main fixation product for As. Dahlgren & Hartford and Bull expects the chromium arsenate to be present as a precipitate, while Pizzi suggests that some may form wood complexes. Dahlgren & Hartford expects some As to be bound to Cu, as mentioned earlier.

## Fixation of Cr

Depending on the CCA formulation (CCA-B or CCA-C) all or a major part of Cr is fixed to As and Cu as described above. In CCA-C formulations there will be some additional Cr that is not fixed to either As or Cu. Pizzi seems to believe that the remaining Cr is present as chromate ( $\text{CrO}_4^{2-}$ ) complexes with wood. Dahlgren & Hartford and Bull are in agreement with each other and states that precipitated  $\text{Cr}(\text{OH})_3$  are the most likely form of the remaining Cr.

## 2.5 Fixation products in summary.

Based on the fixation possibilities mentioned in section 2.4., the most significant final fixation products of CCA in wood seems to be:

**Cu:** ion exchange fixation to wood  
**As:**  $\text{CrAsO}_4$ , precipitated on wood or bound to wood  
**Cr:**  $\text{Cr}(\text{OH})_3$  precipitated on wood and  $\text{CrAsO}_4$

In addition to that, precipitated copper sulphate ( $\text{CuSO}_4$ ) and copper arsenate ( $\text{Cu}(\text{OH})\text{CuAsO}_4$ ) may be present, depending on the CCA formulation.

In the following section, the actual distribution of CCA in impregnated wood will be presented as described in the literature.

## 3. Distribution of CCA in impregnated wood

Several attempts to describe the distribution of CCA in wood can be found in the literature. Different wood species (soft wood and hard wood) has been investigated, with different loadings and CCA formulations. Most of the investigations have been made on freshly impregnated wood with high loadings of CCA.

### 3.1. Electron Microscope examination by Chou et al. 1973

In 1973 Chou *et al.* examined the distribution of CCA in the walls of tracheids of pine wood impregnated with a CCA-C formulation (Tanalith C) to a retention level of 40



kg/m<sup>3</sup>. Both conventional electron microscope examination of ultra thin sections of impregnated wood and “EMMA-4” analysis (electron microscope microanalyses) to determine the CCA concentration in various parts of the tracheid wall were used. The middle lamella, the S2 layer and in the lumen-surface of the tracheids was investigated. At low magnification some coarse crystalline deposits was seen occasionally, but it was not a constant feature in the sections investigated. The coarse deposits seemed to be pure copper compounds and Chou et al. (1973) suggest that it may be basic copper hydroxide  $\text{Cu}(\text{OH})_2$ . At high magnification (99,000:1 and 171,000:1) Chou et al. (1973) found that the lumen surface and the cellulose microfibrils were coated with a thin layer CCA deposit. The lumen surface layer was approximately 20-30 nm thick and consisted of fine granulates about 1.5 nm in diameter. In the S2 layer the surface of each cellulose microfibril appeared to be coated by a layer of metallic deposit about 1.5 – 2.0 nm thick. The EMMA analyses showed that Cu was present in all the sections and that except from the coarse crystalline deposits, Cu was invariably found to be associated with Cr and/or As.

### 3.2. SEM-EDX analyses by Greaves 1974

Greaves (1974) used SEM (Scanning Electron Microscopy) coupled with EDXA (Energy Dispersive X-ray Analysis) to investigate the distribution of CCA in different wood species. Sapwood was impregnated with 3% Boliden K33 to a final loading of approximately 20 kg/m<sup>3</sup> for pine wood. Greaves (1974) found varying amounts of amorphous and crystalline cellular inclusions on the cell wall surfaces. Such deposits were in many cases very numerous and consisted of all the three CCA components but in different ratios to each other. Greaves (1974) also investigated samples that had been leached after the impregnation. In these samples the deposits on the cell surfaces were much less readily observed. Thus the deposits probably consist of water soluble combinations of Cu, Cr and As. Greaves found that after leaching, a redistribution of CCA had taken place. Based on measurement of Cu, Cr and As in different depths of the wood he suggested that in softwood, unfixed material such as the observed amorphous and crystalline deposits were redistributed by elements migrating inwards rather than outwards, thereby providing a better impregnation of the wood.

Greaves (1974) found high concentrations of CCA in connection with pit membranes, including crossfield pits and found this to be in agreement with the main penetration path in soft wood being through the rays.

The Cu:Cr:As ratio differed, but Greaves (1974) did not report of any difference in fixation of the three compounds. This would also be difficult, since the measurements were performed by scanning of surface areas with sizes from approximately 2x2 µm to 20x20 µm.

More recent SEM-EDX analyses of CCA distribution in softwood include the investigations of Matsunaga et al. (2001) and Helsen & Bulck (1998).

### 3.3 SEM-EDX analyses by Helsen & Bulck 1998

In the investigation by Helsen & Bulck (1998) the main purpose was to compare CCA



distribution in wood and its pyrolysis residue. Before pyrolysis Cu, Cr and As are found in both tracheids and ray cells in pine sap wood treated with a CCA-C salt formulation to a retention level of 9 kg/m<sup>3</sup>. The Cu:Cr:As ratio differed in the different locations and this may be an indication of selective fixation of the Cu, Cr and As by the different wood components.

All three CCA components were also detected further away from the surface of the tracheids and also in the middle lamella, with lower concentration of the three metals with increasing distance from the tracheid surfaces. In addition to that, a deposit with high Cu concentration and a non-negligible amount of sulphur was observed on the surface of a tracheid.

### 3.3 SEM-EDX analyses by Matsunaga et al. (2001)

Matsunaga et al. (2001) investigated commercially CCA treated Japanese cedar sapwood and found that Cu, Cr and As were more distributed in ray parenchyma cells than in tracheids and that the element were concentrated in cross field pitting. Matsunaga et al. (2001) also found increased levels of Cr in the parenchyma tissues. In order to explain for this, they raise a very interesting point. In the parenchyma cells polysaccharides may be stored and it is possible that a part of the Cr(VI) is reduced by the alcoholic hydroxyl groups of polysaccharides instead of lignin and cellulose parts of the wood. The presence of storage material in the parenchyma cells is not taken into consideration in the fixation theories described earlier, but since rays only account for a smaller fraction of the wood (5-10%) the possibility of CCA being precipitated or complexed to the storage materials in the rays is believed to be of minor importance.

### 3.4. Summarising conclusion on distribution of CCA in wood

In the experiments presented here, Cu, Cr and As was generally found in all parts of the softwood tissue in varying concentrations. There is evidence of deposits on the lumen surface that seems to be water soluble combinations of all three elements in different concentrations. In addition to that pure Cu deposits, presumably copper hydroxide or copper sulphate were observed in two studies.

There is a clear tendency to higher concentrations of CCA in connection with the ray cells and cross field pits compared to the tracheids. This is generally explained by rays being the main penetration pathway for CCA. Another explanation to the high concentration in rays was presented by Matsunaga et al. (2001) and involved reduction of Cr(VI) by the polysaccharides that are stored in the parenchyma cells.

## 4. Extraction of CCA from wood

In this section the ability to extract CCA from the wood is being investigated. The main focus will be on the ability to extract CCA after the wood has been removed from service since this is the topic of the thesis. However it is apparent that CCA to

some degree will leach from the wood during service. Therefore the concentration of CCA in the wood when it is removed from service will be decreased compared to newly impregnated wood.

CCA is in general considered a leach resistance preservative with potential of resisting biological deterioration for 20 to 50 or more years in service (*Cooper et al. 2001*). Leaching studies of different CCA formulations under different conditions using different methods are numerous.

The use of different leaching tests, with different wood size fractions and loadings, makes it difficult to compare leaching experiments in the laboratory, and when leaching in structures that are still in service are to be evaluated, several other factors like age, construction and site characteristics has to be considered (*Lebow et al. 2004*). In a recent published review on leaching of CCA in aquatic environments *Hingston et al. (2001)* reported that numerous factors affected the leaching rate of CCA, including pH, salinity, temperature and leaching media. It was concluded from the literature that insufficient data exists regarding these effects to allow for accurate quantification of leaching rates.

*Cooper et al. (2000)* reported the residual CCA levels in CCA treated poles that was removed from service after 1-50 years and found that the loading of CCA was above the toxic threshold for decay ( $2.9 \text{ kg/m}^3$ ) in even the oldest poles. They concluded that As appears to be leached more than the other components.

Leaching rates of up to 25% As to soil and water from in-service wood during the first 2-5 years has been reported numerous times in the literature (e.g. *Henningsson & Carlsson 1984, Hansen & Frost 1996*). In an early study by *Evans (1978)* leaching of 20% As was reported to take place within the first 15-20 months of the service life and after that the leaching was low. In general Cr was found to be the most leach resistance of the three elements (e.g. *Taylor & Cooper 2003, Lebow et al. 1999*) and that leaching of CCA could be reduced by treatment with a water repellent (e.g. *Taylor & Cooper 2001, Cui & Walcheski 2000*). The leaching of CCA has also been reported to be lower when a CCA-C formulation is used instead of CCA-B (*Kim & Kim 1993*). This would be the expected since the higher Cr content in CCA-C should ensure stronger fixation of Cu and As.

In the following different extraction attempts to actively remove CCA from wood is addressed based on the found literature.

## 4.1. Extraction by complexing/chelating agents and acids.

*Honda et al. (1991)* investigated the possibility of extracting Cu, Cr and As from CCA treated wood in wood particles. The wood was impregnated one month prior to being crushed and sieved. The size of the wood particles varied from 0-20 mm.

They found that more than 80% of Cu, Cr and As could be removed from the smallest wood particles (<2 mm) after extraction with mineral acids like sulphuric, nitric

and hydrochloric acid, but an undesirable effect of the mineral acids was that varying amounts of organic carbon was also extracted from the wood. *Honda et al (1991)* found that sulphuric acid was the best suited extractor and optimised the extraction to 5 repeated cycles of extraction. Each cycle consisted of one hour extraction in 0.25 N sulphuric acid at 100 °C and L:S 15:1. Under these conditions 96% Cr, 97% Cu and 100% As was removed, corresponding to residual concentrations of 48 ppm Cr, 27 ppm Cu and zero As. Removal efficiencies and residual concentrations were seemingly based on measurements of residual CCA in less than 1 g wood.

*Kazi and Cooper (1998)* tested 13 organic and inorganic leaching agents ability to remove CCA from CCA-C treated wood particles (< 850 µm) made from out-of-service wood. The experimental conditions were 6 hours extraction at 50°C, L:S ratio 15:1 and the concentration of the leaching agent was 10%. They founds that oxalic acid could remove 100% Cr, 91% As but only 55% Cu, whereas formic acid and citric acid removed 100% Cu but 66-76% of Cr and As. A combination of 5% oxalic acid with either 5% formic or citric acid resulted in 90-97% removal of Cr and As but only 49-60% Cu. Instead *Kazi & Cooper (1998)* investigated sequential extraction with 2 hours extraction in one of the acids, followed by similar extractions in another acid. They found that the order of extraction was very important to the removal of Cu but did not affect the removal of Cr and As. When the wood particles was extracted by oxalic acid first, followed by either formic or citric acid 81-85% Cu was removed and 89-95% Cr and As. If the order of extraction was reversed (citric or formic acid before oxalic acid) then 100% Cu was removed and 86-95% Cr and As. They did not propose any explanation as to why the extraction order influenced the removal of Cu. Mineral acids like sulphuric, nitric, hydrochloric and phosphoric acid removed 82-100% of Cu, Cr and As but was considered unpopular due to high extraction of total organic carbon (TOC) based on the findings by *Honda et al. (1991)*. *Kazi & Cooper* also investigated alkaline extraction of CCA and found that 10% sodium hydroxide could remove 91% As but only 18% Cr and 33% Cu. Residual concentrations of Cu, Cr and As could not be obtained based on the information given in the paper by *Kazi & Cooper (1998)*.

In a different study by *Kazi & Cooper (1999)* hydrogen peroxide was used as an extraction agent in experimental conditions similar to the above mentioned (*Kazi & Cooper 1998*). They found that 10% hydrogen peroxide could remove 94-98% of Cu, Cr and As, resulting in residual concentrations of 140 ppm Cu, 410 ppm Cr and 115 ppm As. In addition they found that the solution containing the extracted CCA could be mixed with new CCA in a ratio 1:1 and reused to impregnate new wood. Cr in the extracted CCA is in the form of Cr(III) and was therefore oxidised with dilute aqueous hydrogen peroxide at elevated temperature (>80 °C) and low pH to chromate (Cr(VI)) before mixing. The 1:1 mixture of recovered and new CCA was compatible with freshly prepared CCA-C solution in both fixation and leaching tests.

*Kartal (2003)* investigated the extraction efficiency of EDTA (ethylenediaminetetraacetic acid) in the removal of CCA-C from different wood waste fractions. CCA-C

treated wood with a retention level of 21 kg/m<sup>3</sup> was obtained from a preservative treatment plant and from the sapwood part three different wood fractions was made: sawdust (<420 µm), chips (10-17 mm longitude, 0.15-0.35 mm transverse) and blocks (19x19x19 mm). A 24 hours extraction with 1% EDTA at L:S 10:1 resulted in removal of 93% Cu, 36% Cr and 38% As from sawdust, corresponding to residual concentrations in the wood of 686 ppm Cu, 10,560 ppm Cr and 8556 ppm As (calculated from *Kartal 2003*). When wood chips was used instead, 60% Cu, 13% Cr and 25% As was removed and in similar leaching experiments with wood blocks only 19% Cu was removed and the removal of Cr and As was less than 5%. Based on the results *Kartal (2003)* concludes that EDTA is most suitable for the removal of Cu and that removal of Cu is increased with decreasing wood size.

In a study by *Kartal & Kose (2003)* both single and dual extraction of CCA by EDTA, oxalic acid and NTA (nitrilotriacetic acid) was investigated for wood chips and sawdust equal to the above described (*Kartal 2003*). They found that the highest removal was obtained by dual extraction (L:S 10:1) with 1% EDTA and 1% oxalic acid but that the order of acid was not important. In sawdust 100% Cu and more than 90% Cr and As was removed, resulting in residual concentrations of 1650 ppm Cr and 1380 ppm As (calculation based on *Kartal 2003*). In wood chips approximately 90% Cu and 80-85% Cr and As was removed.

*Kamden et al (1998)* investigated the possibility of removing CCA from larger pieces of wood in order to avoid chipping and grinding poles into wood particles or sawdust. Both 20 year old waste wood and freshly impregnated poles were used in the experiments and different wood size fractions, from < 2 mm particles to 30 cm pole sections were investigated.

The wood was placed in a pressure cooker and after initial vacuum an extraction solution that contained both citric acid and EDTA was injected and the experiment was conducted at 100 °C. The used concentrations of the acids were not cited by the authors. The duration of the experiments varied according to wood size. Pole sections (31 cm long, 23 cm diameter) were extracted for 54 hours, lumber (12.5 x 5 x 2.5 cm) for 58 hours. The L:S ratio in the experiments varied between 10:1 and 60:1. The L:S ratio used in the experiments presented here is unknown. From pole sections 98% Cu, 96% Cr and 95% As was removed, resulting in residual concentrations of 94 ppm Cu, 476 ppm Cr and 380 ppm As. From lumber removal efficiencies of 98% Cu, 96% Cr and 100 % As was obtained. This resulted in residual concentrations of 59 ppm Cu and 178 ppm Cr. Residual concentrations of CCA were calculated from information's given by *Kamdem et al. (1998)*.

## 4.2. Biological extraction by oxalic acid producing fungi

In Germany *Stephan & Peek (1992)* investigated the possibility of biological detoxification of CCA treated wood. They used a brown rot causing fungi that primarily produced oxalic acid. Pine sapwood was impregnated with CCA for the purpose of this investigation (8-20 kg/m<sup>3</sup>). After 16 weeks of incubation with the fungi, the samples

were leached with demineralised water and the concentration of Cu, Cr and As was measured in the leachate. Based on this, 60-75% As, 50-60% Cr and less than 10% Cu was removed. No residual concentration of Cu, Cr and As could be calculated based on the information provided in the paper. The low removal of Cu was attributed to the limited solubility of copper oxalate (CuOx) and SEM studies of the wood revealed crystals that were most likely copper oxalate. By optimising the process with regard to pH, a 20% removal of Cu was obtained from CC treated wood in the laboratory. After further optimisation the method was also tried in a scale-up experiment with 4 m<sup>3</sup> wood chips (*Leithoff & Peek 1997*). However, an industrial application was deemed unlikely due to high costs and problems with contamination of the system (*Leithoff & Peek 1998*).

### 4.3. Dual extraction by oxalic acid and metal tolerant bacteria

*Clausen (2000)* describes a two-step remediation process, which involve a combination of oxalic acid (0.8%) extraction and bacterial culture with a metal-tolerant bacterium. In this dual remediation process 97% Cu, 78% Cr and 93% As was removed from wood wafers (1.9 cm x 1.9 cm x 0.32 cm) that was impregnated with CCA for this experiment. After the remediation the concentration of Cu, Cr and As in the wood was 75 ppm, 893 ppm and 150 ppm respectively (calculated from *Clausen 2000*).

*Clausen (2004a)* found that a L:S ratio of 100:1 (v/w) of oxalic acid to wood, the oxalic acid could be used for three repeated extractions with no decrease in the removal efficiency of Cu, Cr and As. In this experiment, wood particles of size 1-3 mm were used. The use of the bacterial culture makes the process costly, since the growth medium accounts for 99% of the total chemical costs in the process. Efforts are being made to reduce this cost (*Clausen 2004b*).

### 4.4. Extraction by a combination of steam explosion and different acids

*Shiau et al. (2000)* compares two processes where the CCA is extracted by steam explosion and by different acids (citric, acetic and sulphuric acid). In steam explosion the wood (as chips) are placed in a pressure reactor (max pressure app. 3100 kPa and max. temperature 220 °C) with an active steam flow during hydrolysis. The release of steam causes the matter to explode into a fibrous mass. Three year old samples of decking (pine wood) were used in three different size fractions. The best results were obtained when wood particles (0.2 mm) were extracted with citric acid for 21 days. Here 81% Cr, 84% Cu and 87% As was removed. The final concentration in the wood after the extraction was 998 ppm Cr, 329 ppm Cu and 520 ppm As. Steam explosion did not increase the extractability.

### 4.5. Extraction by liquefying of wood

In a study by *Lin & Hse (2002)* the possibility of removing CCA by liquefying the wood was investigated. The wood was new impregnated wood and was reduced to sawdust before liquefying in a mixture of polyethylene glycol and glycerine with sulphuric acid as a catalyst. The liquefaction took place at 150 °C in a sealed container for two

hours with L:S ratio of 3:1. CCA was removed from the liquid by complexing (by iron sulphate) and precipitation (by calcium hydroxide,  $\text{Ca}(\text{OH})_2$ ) and *Lin & Hse (2002)* found that the best results was obtained by adding iron sulphate ( $\text{FeSO}_4$ ) during the liquefaction. Removal efficiencies of 86% Cu and Cr and 92% As was obtained. No information could be found on the residual concentrations of CCA in the wood.

#### 4.6. Summarising conclusions on extraction of CCA from wood

In the experiments presented here different attempts were made to extract Cu, Cr and As from CCA treated wood by acids, NaOH, complexing agent (in acid environment) and by bacteria or fungi. In some cases elevated temperature and pressure was part of the extraction experiments and in the cases of steam explosion and liquefaction the wood structure was destroyed. The L:S ratio varied from 3:1 to 100:1 and removal efficiency increase with increasing L:S ratio. Most experiments were made with small wood particles and in general it was found that the removal of CCA decreased with increasing wood size fraction but in the case of removal of CCA from pole sections and boards it was reported that equal high removal could be obtained if the duration of the experiments were increased. Removal efficiencies of 20-100% Cu, 36-96% Cr and 38-100% As was reported. In most cases residual concentrations of Cu, Cr and As in the wood after extraction was either given in the paper or could be deducted from information of initial concentrations in the wood. Residual concentrations of 0-686 ppm Cu, 48-10,560 ppm Cr and 0-8556 ppm were reported.

Apart from the extraction with NaOH, all the extractions were done at acidic pH. Mineral acids were able to remove large amounts of all three CCA components, however they seemed to also extract organic carbon (TOC) to a large extent. Organic acids, that may also function as complexing agents were tested and high removal efficiencies were obtained with oxalic, citric and formic acid in different combinations. Oxalic acid was found to be suited for removal of Cr and As whereas high removal of Cu was not obtained by oxalic acid alone. EDTA alone was suited for the removal of Cu but not Cr and As. EDTA in connection with either oxalic or citric acid removed a high percentage of all three CCA components.

Initial loadings of CCA varied due to the use of new impregnated wood with different loadings and actual waste wood where the concentration of CCA most likely is reduced due to leaching during service. Due to the variations in initial loading it seems evident that the residual concentrations are compared, rather than the percentage removal. For instance *Kartal & kose (2003)* used new impregnated wood with an initial loading of 21 kg/m<sup>3</sup> and even though they reported more than 90% removal of As, the residual concentration was 1380 ppm. In the investigation reported by *Shiau et al. 2000*, three year old decking was used and here the removal of As was 87% but the residual concentration of As was only 520 ppm.

#### 5.0. Summarising conclusions

CCA has been used extensively for wood preservation worldwide. It has been banned



for use in Denmark since 1993 but the long service life of CCA treated wood (20-50 years) makes it apparent that CCA will be present in the wood waste in many years to come. CCA exists in many different formulations, but they may be divided into three categories: CCA-A, CCA-B and CCA-C depending on the ratio of Cu, Cr and As. CCA-C was reported to be the most used formulation at present because it is considered to be most leach resistance.

In the found literature of the CCA fixation mechanism there is a general acceptance that the reduction of Cr(VI) to Cr(III) is the driving force of the fixation of CCA and that the main fixation products are Cu fixed by ion exchange to the wood components (presumably with a higher affinity for lignin compared to cellulose) chrome arsenate and chromium hydroxide. There is some disagreement concerning the presence of Cr(VI) in fully fixed wood but analyses of the reduction process seems to favour total reduction of Cr(VI) (*Kaldas & Cooper 1993*).

In the found literature it was difficult to verify the presence of the exact above proposed fixation products in wood. Several analyses, especially SEM-EDX analyses, have been performed on CCA impregnated wood in order to investigate the micro distribution of Cu, Cr and As in the wood. In general all three components are found to be distributed in all the sap wood but in different concentrations. The concentration of CCA seemed to be higher in the ray cells and cross field pitting compared to the tracheids. This is often associated with the fact that rays are the main pathway for CCA penetration. However, the presence of polysaccharides in the parenchyma cells that may reduce Cr(VI) may also be of importance. In the fixation theory proposed by Dahlgren & Hartford and Pizzi, the different chemical constituents of the parenchyma cells are not taken into consideration.

Laboratory studies of the degree of leaching of CCA during use are numerous, but the use of different tests and conditions makes it difficult to compare the results. In general Cr was found to be the most leach resistant of the CCA components. Several factors like the use of water repellent and change of formulation from CCA-B to CCA-C was found to decrease leaching. In CCA-C the molar ratio of Cr compared to Cu and As are higher than in CCA-B

Several investigations have been reported on the subject of actively removing CCA from wood. Even though these investigations are often initiated by a desire to solve the waste problem that may occur from the use of CCA treated wood, many of the experiments sited here were made with new impregnated wood, either impregnated for the purpose of the study or obtained directly from a wood preservation plant. In all but one experiment, acidic conditions were used. Alkaline conditions were found to be suited for the removal of As only. High removal of CCA was obtained with mineral acids and in the case of many repeated extraction cycles with sulphuric acid, residual concentrations below 50 ppm of all three components were reported. The use of organic acids and chelating agents like EDTA was preferred by most authors, one of the reasons being that high extraction of organic carbon (TOC) was associated with the use of mineral acids. In general good results were obtained with citric, oxalic and formic acid and EDTA in different combinations.



Often the obtained CCA removal is only sited in percentage of Cu, Cr and As removed of initial amount, but given the fact that different loadings of CCA were used, percentage may not be the most suitable parameter to uses when different studies are compared. When possible, residual concentrations of Cu, Cr and As after extraction are given or calculated from available information, in order to allow for a more meaningful comparison. In the end the actual concentration of CCA in the wood after extraction, rather than the percentage of the initial amount that was removed determine the possible fate of the wood after remediation. In addition the difference between new impregnated wood and waste wood must be considered. When new wood is used there is a possibility of poor CCA fixation in parts of the wood or on the surface, a fraction that presumably is easier to extract compared to the remaining properly fixed CCA. Leaching of CCA is not in steady state during the service life, leaching is higher in the beginning of the service life which implies that there is a CCA fraction that will be easy to remove in new wood. In waste wood this CCA fraction may already be leached, depending on the life span of the wood and the CCA present. In waste wood the removal of CCA may even be more difficult due to the stronger fixation.

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## 4 Wood used in experiments

Two waste wood fractions were used in the experimental work presented in this thesis; an electricity pole, and a mixture of waste wood from a recycling company. The known characteristics and concentration of Cu, Cr and As in the wood are presented here. The concentration of Cu, Cr and As is measured by AAS (Atomic Absorption Spectroscopy) after microwave assisted acid digestion. See Chapter 5 (Experimental section) for further details.

### 1. Pole

An out of service electricity pole that was removed from service in 1999 was obtained from NESÅ, a large Danish electricity company. The pole came from a series of poles that was being replaced by cables in the ground and was not removed due to decay. Two significant nails are found on all treated electricity poles in Denmark. On these nails preservation codes are given that provides precise information's regarding the impregnation of the pole. The pole in question was impregnated in 1962 by Collstrop A/S. The pole is common spruce or Norway spruce (*Picea abies* L.) and it is impregnated by 12 kg K33 (CCA-B) per m<sup>3</sup> sapwood.

The sapwood fraction of a pole is approximately 50 % and the remaining 50% is heartwood, which is not impregnated. Instead of chipping the whole pole, a chainsaw was used to cut off the outermost 3 cm of the pole and only this fraction was chipped. The diameter of the pole was approximately 20 cm and with a 50% sapwood fraction, this fraction would be the outermost 3 cm.

The wood was chipped in a conventional shredder after all metal pieces (nails etc) had been removed from the wood. The size of the wood chips varied between 1-5 cm in the longitudinal direction and 0.1-1 cm in the transverse directions.

Chips were made from both the sapwood fraction above ground and the sapwood fraction that had been placed below ground when the pole was in service due to the large difference in concentration.

In table 1 the concentrations of Cu, Cr and As are given for both fractions.

**Table 1:** Concentration of Cu, Cr and As in sapwood fraction of pole. Mean value  $\pm$  95% CL

	Above ground		Below ground	
	ppm*	$\pm$ 95% CL	ppm*	$\pm$ 95% CL
[Cu]	426	265	1549	233
[Cr]	837	299	1636	218
[As]	589	658	1863	701

Mean concentration based on 4 measurements above ground and 15 below ground. (3 and 6 for As)

\*(mg per kg dry wood)

The large 95% confidence limits for the three CCA components may be taken as an indication that the concentration of CCA (as Cu, Cr and As) varies in the wood, however it must also be emphasised that the number of replicates were limited, especially for As. The possible presence of small fractions of (untreated) heartwood may also contribute to the variation in CCA between the samples.

The concentration of Cu, Cr and As is radically higher in the wood below ground compared to above ground. There are some observations in the literature that CCA is redistributed downwards during use (e.g. *Hainey et al. 1989*) but this is not expected to be the main reason for the observed difference in concentration between top and bottom of the pole. Instead the difference is mainly attributed to the impregnation method. In the Gewecke or Saug-Kappe method that was the sap displacement method most likely used by Collstrop A/S in 1962 when the pole was treated (*Richardson 1993*), a cap is fitted to the top end of the pole and a vacuum is applied to remove the sap and induce preservative flow from a reservoir at the butt end of the pole (*Richardson 1993*), thereby a concentration difference between top and bottom may be induced. In other sap displacement methods caps are fitted to both ends and the preservative are introduced radial instead of longitudinal (*Miljøstyrelsen 1992*). In this method no difference in the CCA concentration between top and bottom is expected.

The Cr:Cu:As ratio in the wood chips are 2:0.9:1 above ground and 1.3:1:1 below ground. This differs from the average mole ratios for CCA-B formulations (0.9:0.6:1, as described in *Chapter 3 CCA in wood*). It must be emphasised that the molar ratio of Cr, Cu and As presented for CCA-B formulations may vary since it is based on the average content of the three compounds in the formulation. However, it seems evident that the leaching is more pronounced for Cu and As compared to Cr. This is in agreement with the finding in the literature (e.g. *Taylor & Cooper 2003, Lebow et al. 1999*)

Wood chips from the pole were only used in laboratory experiments.



## 2. Mixed wood

The mixed wood fraction was obtained from RGS90 and was considered to be representative of mixed treated waste wood in general.

From a large pile of demolition waste wood, approximately 10 m<sup>3</sup> impregnated wood was collected. The wood was separated after identification of the presence of Cu in the wood. The identification was conducted with Chromazurol S, a colour reagent that turns blue in contact with Cu. (described in: *Solo-Gabriele et al. 1999*). The presence of Cu in wood is a strong indication that it has been impregnated, but does not reveal if it is impregnated with CCA or another preservative that contains Cu.

Most of the wood appeared to be old weathered wood but a fraction of the wood seemed to be newly impregnated with the significant green colour that indicates wood impregnated with Cu. This wood was most likely cut offs from a production site and had not been subjected to weathering (and leaching) before it turned up as waste. The waste wood was present in many different forms and dimensions, e.g. boards and what appeared to be parts of poles. The large variations also mean varying heartwood fractions. No effort was made to separate the sapwood and heartwood prior to the chipping, since this would be a difficult and time consuming process that is not foreseen to take place in an industrial size operation.

After the identification with Chromazurol S, the wood was shredded and the wood chips were subjected to magnetic separation to remove pieces of metal (nails etc). Finally the wood was divided into three size fractions (Fine (F): < 2 cm, Medium (M): 2-4 cm and Large (L): > 4cm) by sieving. The shredding and sieving processes took place at RGS90 using their industrial size facilities.

In table 2 the concentration of Cu, Cr and As in the wood chips are given.

**Table 2:** Concentration of Cu, Cr and As in mixed wood. Mean value ± 95% CL

	ppm*	± 95% CL
[Cu]	1279	66
[Cr]	1334	91
[As]	837	114

Based on 179 measurements for Cu and Cr, 95 measurements for As.

\*(mg per kg dry wood)

The confidence limits obtained for the mixed wood is much lower than those obtained for the pole. The main reason for this is most likely the high number of replicates as opposed to low variation between the samples. The large variation in wood forms and dimensions makes variations in concentration of Cu Cr and As inevitable. A comparison of the molar ratios of Cu, Cr and As to the different CCA formulations is not reasonable in this case due to the mix of many different types of wood products, probably both for use above and below ground and both weathered wood and cut offs from newly impregnated wood. In addition to that there is probably also different wood species, most likely the softwood species pine and spruce, since these are the most common species used for impregnation in Denmark. All these factors would influence the concentration of Cu, Cr and As in the wood. The presence of newly impregnated cut offs would also suggest that part of the wood does not contain As (or even Cr), since As has been banned as a wood preservative in Denmark since 1993 (*Hansen et al 1997*) and in 1997 the use of Cr for wood preservation in Denmark was stopped. (*Andersson & Quistgaard 2002*).

Mixed wood was used for laboratory experiments as well as pilot scale experiments.

### 3. Summarising conclusions

Three different waste wood fractions has been chipped and used for the experimental work presented in this thesis. In table 3 the concentration of Cu, Cr and As in the wood chips are presented.

Table 3: Concentration of Cu, Cr and As in different waste wood fractions. Mean value  $\pm$  95% CL

	[Cu] <sub>ppm</sub> $\pm$ 95% CL	[Cr] <sub>ppm</sub> $\pm$ 95% CL	[As] <sub>ppm</sub> $\pm$ 95% CL
Pole above ground	426 $\pm$ 265	837 $\pm$ 299	589 $\pm$ 658
Pole below ground	1549 $\pm$ 233	1636 $\pm$ 218	1863 $\pm$ 701
Mixed wood	1279 $\pm$ 66	1334 $\pm$ 91	837 $\pm$ 114

All the wood was regular waste wood and was judged as representative for waste wood in general. In the mixed wood newly impregnated cut offs was present and this is also expected to account for a part of the waste wood in general. *Evans (2001)* estimated the cut offs to represent 5% of the annual production.

Only in the pole was the heartwood separated from the sapwood – this is the only fraction that is likely to be treated this way in an industrial scale, since the ratio is high 50:50 and poles represent a uniform waste fraction and each pole has a significant volume. By separating the heartwood and sapwood in poles, the amount of pro-

blematic waste is cut in half, since the heartwood is not impregnated. The heartwood may be reused or even incinerated and the sapwood is the only part that needs to be remediated.

In the mixed waste wood a fraction of the wood will be heartwood but separation is not likely in an industrial size operation, since the diversity of the wood products will make it a difficult and time consuming process.

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# 5 Experimental Section

In this chapter the general experimental conditions and the optimisation process for the electrochemical remediation method based on laboratory experiments are described. The methods and conditions described here apply to all experiments presented unless otherwise noted.

## 1. Measuring concentrations of Cu, Cr and As by AAS

The concentration of Cu, Cr and As was measured by atomic absorption spectroscopy (AAS) in flame.

Prior to AAS wood samples were subjected to acid digestion (*see below*) and aqueous samples were preserved with 16M nitric acid ( $\text{HNO}_3$ ) and a sample to acid ratio of 4:1.

Cu and Cr was measured by AAS in flame (Model GBG 923)

The measured absorbance in the samples were translated into concentration (ppm) by a calibration curve of six standards that span the linear region. In the case of Cu and Cr the absorbance is directly proportional with the concentration from 0.5 ppm to 5 ppm. All samples, including the standards had a  $\text{HNO}_3$  matrix and the blank sample that was used for calibration of the system consisted of 0.1 M  $\text{HNO}_3$ . The same concentration of  $\text{HNO}_3$  was used to dilute samples to concentrations that were within the linear region.

As was measured by AAS in flame (Perkin Elmer 2100) Sample preparation was the same as for Cu and Cr. As was measured from 0 to 100 ppm.

Arsenic analyses were conducted at external laboratories and not all samples were analysed for As. Normally As was only measured in experiments where removal of Cu and Cr was promising. The fact that As had to be measured outside the department made the analysis less frequent and more expensive than the Cu and Cr analyses. In general it was found that As was easy to remove and when the wood was analysed for As after remediation, high removal of As was obtained.

Based on this it was decided that it would be acceptable to only measure As in selected experiments.

## 2. Acid digestion of wood samples

Cu, Cr and As were measured after acid digestion of the wood.

Initially the procedure was the same as used for soil samples, where the acid digestion took place in an autoclave according to Danish Standard DS259. This however was not a suited method for acid digestion of wood. The high content of organic matter in wood resulted in a massive pressure build up inside the screw capped flasks (DURAN® glass) that contained the wood sample and the HNO<sub>3</sub>. In one case the pressure was so high that one autoclave flask broke during the digestion, causing the sample to be lost and the autoclave damaged. After that the digestion was performed in a microwave where the pressure could be controlled.

2.1. Microwave assisted acid digestion

A microwave (model CEM MDS-2000, 630 watts) was used for these investigations. A total of 12 samples could be digested simultaneous, however in practice no more than 4-6 samples were normally digested at a time. The programme: Acid digestion of wood pulp in a closed vessel using pressure controlled micro wave heating for the determination of metals by spectroscopic methods, was optimised to wood chips and the experimental conditions concerning the programme are outlined in table 1.

Table 1: Programme for microwave assisted acid digestion of wood chips.

Programme stage	1	2	3	4
% Power	80	80	80	80
Pressure, PSI*	40	85	135	175
Time (min)	10	10	10	10
TAP** (min)	5	5	5	5
Fan speed (%)	100	100	100	100

\*PSI: Pounds per square inch. (lb/in<sup>2</sup>) \*\*TAP: Time at set parameters of pressure.

No more than 0.4 g wood was weighed into each vessel (Teflon coated) and 10 ml HNO<sub>3</sub> (16 M) was added. In some cases 0.4 g wood was too much and the digestion failed. In these cases new digestions were conducted with 0.25 g wood in each vessel. Following the digestion the samples were vacuum-filtered on nucleopore filters (0.45 µm) and diluted to 25 ml with distilled water.

Visual investigation of the filters suggested that the digestion was not total, since a small layer of a light yellow/white matter was found to be left on the filter following the filtration.

There was a potential risk that some Cu, Cr and As was retained in the residue but an attempt to liquefy this matter by introducing an additional sequence to the microwave programme where hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were added to the samples after the initial digestion with HNO<sub>3</sub>, let to no statistically significant increase in the measured

concentration of Cu, Cr and As after digestion. A residue was still observed on the filter after digestion with  $\text{H}_2\text{O}_2$  and it was decided not to use  $\text{H}_2\text{O}_2$  in the digestion of wood samples, since apparently no additional Cu, Cr and As was gained by introducing a step that prolonged the procedure by extra handling of the samples and an additional micro wave assisted digestion circle.

## 2.2. Preparation of wood sample for acid digestion.

Since the amount of wood to be used in each digestion was limited (0.25 – 0.4 g) efforts were made to try to ensure the samples were representative of the wood to be tested. In most cases the batch of wood chips to be investigated were mixed manually and samples were taken from different parts of the batch and mixed again. From this batch a series of individual wood chips, varying in size, shape and colour, were taken. Each chip was cut into small pieces with a knife and after mixing the small pieces, samples were taken from this. In each sample (0.25 -0.4 g wood) several wood pieces was used.

# 3. Extraction experiments

During the work in the laboratory, extraction experiments were done in order to evaluate the usefulness of different additives for the EDR process.

The duration of the extraction experiments were 24 hours and after the extraction the samples were vacuum-filtered on nucleopore filters (0.45  $\mu\text{m}$ ) and conserved with  $\text{HNO}_3$  (16 M) before the concentration of Cu and Cr (and in some cases As) was measured by AAS. Extraction experiments were always made in duplicates and most often in triplicates.

## 3.1 Liquid to solid ratio

The liquid to solid ratio (L:S ratio) in the extraction experiments were 6:1. This was similar to the L:S ratio in the middle compartment during the EDR experiments where the wood was not soaked prior to the remediation and also similar to the L:S ratio during soaking in the EDR experiments where the wood was soaked prior to EDR. In the experiments where the wood was soaked prior to the remediation, the L:S ratio in the middle compartment during EDR was less, since the wood was already saturated with the additive.

Generally the extraction experiments consisted of 5 g wood chips mixed with 30 ml liquid in screw capped 100 ml plastic bottles. The dry wood would take up part of the liquid during the extraction and in an experiment with 5 g wood and 30 ml liquid, normally the volume of the free liquid would be reduced to 15-17 ml after the extraction. In order to ensure that the wood chips were covered with liquid all during the extraction, longer chips has to be divided to a maximum length of 30 mm, which corresponds to the diameter of the plastic bottle.

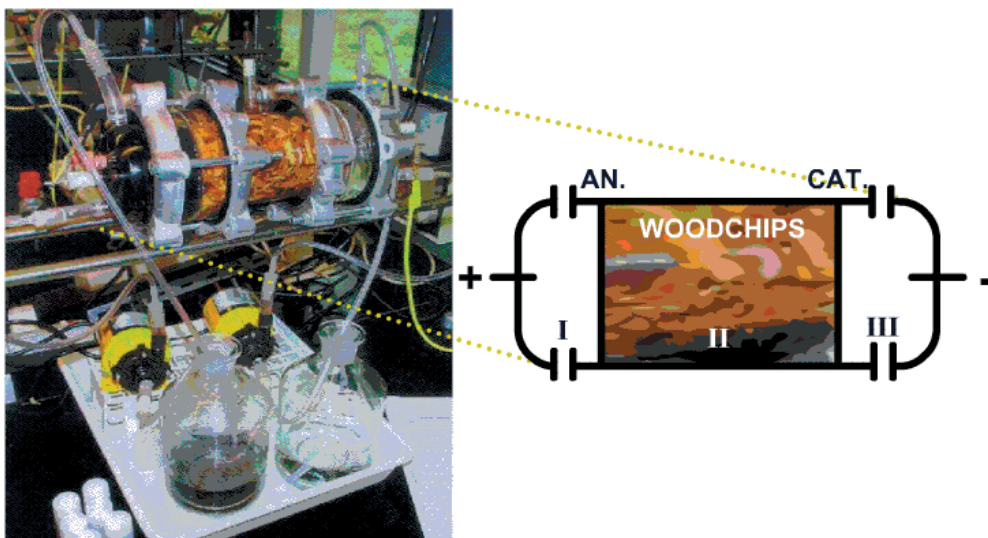
## 4. Electrodialytic remediation experiments

Two different types of electrodialytic remediation (EDR) experiments were carried out. In the initial setup, the dry wood was placed directly in the middle compartment of the EDR cell and covered with an additive, e.g. oxalic acid. In the modified setup, to be used in most of the experiments, the wood was soaked in the additive prior to EDR and the wood chips were covered with water during EDR.

In this section the general experimental conditions for EDR is described first and then the optimisation of the soaking process is described.

### 4.1. Preparation of EDR (setup)

In figure 1 an EDR setup in laboratory scale is illustrated. The laboratory cells were made of glass or Plexiglas. In the laboratory experiments the wood is placed in the middle compartment, a cylinder with an internal diameter of 8 cm. The length of the cylinder varied between 5-15 cm but most experiments were performed with a 10 cm long cylinder.



**Figure 1:** EDR setup. Compartment I and III is the anode and cathode compartment respectively, the wood chips are placed in compartment II. AN: Anion exchange membrane, CAT: Cation exchange membrane.

After the wood is placed in the middle compartment, liquid is added to fill the compartment.

The middle compartment was separated from the anode compartment by an anion exchange membrane and from the cathode compartment, on the other side, by a cation



exchange membrane.

Membranes from both Ionic (anion membrane: AR204SZRA and cation membrane: CR67,HVY,18X40) and Membranes International (AMI-7001 Anion membrane and CMI-7000 Cation membrane) was used.

In each electrode compartment 1 L electrolyte solution was circulated by a Pan World Magnet Pump (5H-5PX). In most cases 0.01 M sodium nitrate ( $\text{NaNO}_3$ ) adjusted with  $\text{HNO}_3$  to pH 2 was used as electrolyte.

The electrodes were platinum coated titanium electrodes from Permascand. The power supply used in the laboratory scale experiments was a Hewlett Packard (E3612A).

## 4.2. During EDR

During the EDR experiments, pH was measured in the electrolytes on an all most daily basis and kept just below pH 2, adjusting with small quantities of concentrated  $\text{HNO}_3$  if necessary. Both pH strips (Whatman®) and a pH electrode from Radiometer, Denmark (PHC2401-8) were used. In some cases 20 ml samples of the electrolyte solution were taken from each electrode compartment and replaced with a similar volume of the original electrolyte solution. Samples were never taken before pH was adjusted. The samples were used to monitor the removal of CCA, by measuring the concentration in the electrolytes as a function of time.

In all experiments the current was kept constant and the voltage was allowed to vary in the span set by the power supply. Situations where the voltage was approaching the limit set by the power supply (approximately 133-137 V in the laboratory scale) was sought to be avoided since it must be considered a system out of control. If the voltage approached the upper limit, the current was reduced or the experiment was terminated.

## 4.3 After EDR

Immediately after the electric power was disconnected at the end of an experiment, the electrode compartments were drained and the EDR cell was disassembled. The wood was dried (48 hours at 50 °C ) before acid digestion of samples according to section 2.

Electrodes were placed in 5 M  $\text{HNO}_3$  and membranes in 1 M  $\text{HNO}_3$  for 16-24 hours to release potential content of Cu, Cr and As. Samples were taken from both electrolytes and the liquid in the middle compartment.

The concentration of Cu and Cr (and in some cases As) were measured in all samples according to *section 1*.

# 5. Optimisation of EDR

During the experimental work several attempt was made to optimise the removal of

CCA from wood by EDR. In the present section two optimisation processes and the obtained results are presented. First the introducing of a soaking period before EDR made it necessary to investigate the optimal duration of the soaking. The second optimisation is the optimisation of the electric field that is applied during EDR. This investigation is primarily based on the experiments in larger scale.

## 5.1. Duration of soaking prior to EDR

In an attempt to optimise the EDR process, it was decided to soak the wood in the additive prior to EDR and use water in the middle compartment during EDR. The expected benefits and reasons for introducing soaking are presented in Chapter 6 (*Results*). The focus in the present chapter is on the experimental optimisations of the duration of the soaking process.

A series of five experiments were conducted in order to determine the optimal duration of the soaking.

### Experimental conditions

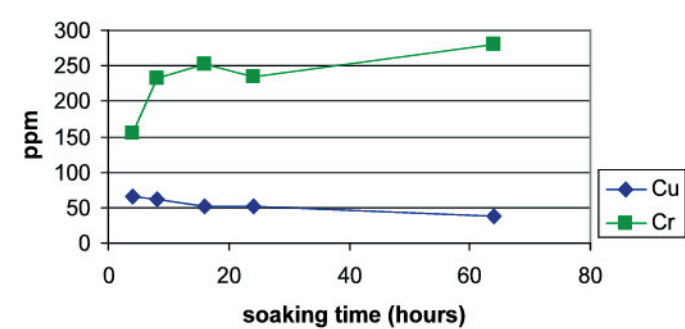
Prior to EDR the wood was soaked in 5% oxalic acid for 4, 8, 16, 24 and 64 hours. Experimental conditions for the five experiments can be seen in table 2 and only the duration of the soaking differed. The wood chips were from the pole, the part below ground (See chapter 4 for further details on the wood)

Table 2: Experimental conditions in experiments for determination of soaking period

Wood (mass)	70 g
Duration	3 days
Liquid in middle compartment during EDR	Water
Electrolytes (anolyte and catholyte)	1 L 0.01 M NaNO <sub>3</sub>
Current	30 mA

### Results and discussion

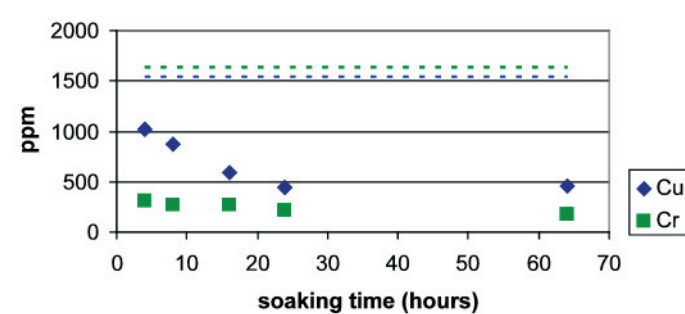
After soaking the final concentration of Cu and Cr was measured in the soaking solution and the results are illustrated in figure 2. The concentration of Cr generally increases with duration of soaking, but the highest increase is seen during the first 16 hours. For Cu the concentration decreases slightly as a function of soaking time. This is most likely due to precipitation of copper oxalate, CuOx (CuC<sub>2</sub>O<sub>4</sub>) that has a low solubility ( $K_{sp} = 4,43 \times 10^{-10}$ , *Chang 1992*) and is not necessarily to be taken as an indication of decreasing removal of Cu with increasing soaking time.



**Figure 2:** Final concentration of Cu and Cr in the soaking solution

Based on the results in figure 2, the optimum soaking period in the case of Cr may be even more than 64 hours - on the assumption that time is not an issue. For Cu the optimum soaking period is depending on where the precipitated CuOx are located. If the majority of the precipitation is taking place outside the wood, in the soaking solution, then the removal of Cu from the wood may increase with time, favouring a long soaking period. If CuOx precipitates mainly inside or on the wood, then the soaking time should not be increased, since Cu is not removed from the wood.

A more precise evaluation of the optimum duration of soaking may be obtained by measuring the removal of Cu and Cr after EDR and in figure 3 the final concentration of Cu and Cr in the wood after EDR is shown.



**Figure 3:** Cu and Cr in wood after remediation as a function of soaking time. Dotted lines indicate initial concentration.

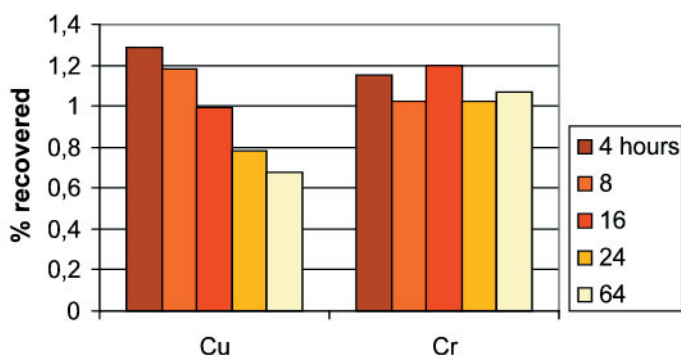
After remediation the concentration of Cu and Cr was reduced in all experiments. The concentration in the wood after remediation decreased with increasing soaking time up to 24 hours. The trend was most obvious for Cu, where the concentration decreased by approximately 50% when the soaking was increased from 4 to 16 hours. By

increasing the soaking time to 64 hours the concentration did not decrease significantly.

Based on the measured concentrations in the soaking solution (see figure 2) it was not possible to determine if CuOx precipitated in the solution or in/on the wood. If the recovery rates of Cu after EDR are compared instead, as is the case in figure 4, then the answer seems to be that CuOx is precipitated in the solution and not in the wood.

Recovery rates for Cu and Cr were determined in all experiments by comparing the initial amount of metal present in the wood with the amount that was recovered after remediation. Initial amount was determined from the measured initial concentration in the wood and the amount of wood used in the experiment. After remediation the amount of Cu and Cr was determined in all liquid phases (in the middle compartment and in the electrolytes, including samples that were taken during the remediation) as well as in connection with the electrodes and membranes and in the wood.

Recovery rates would vary from 80-120% without any apparent reasons, given the large variations in the wood. However under normal conditions an experiment with recovery rate of 68% as is the case for Cu in the experiment after 64 hours soaking would be rejected if no explanation was present.



**Figure 4:** Recovery (% of initial) of Cu and Cr after EDR as a function of soaking time (hours)

The recovery of Cu decreases with increasing soaking time, while the recovery of Cr seems to be unaffected by the soaking time. This is in agreement with the fact that Cu rather than Cr precipitates with oxalic acid. If the precipitation took place inside the wood, then it is assumed that the recovery rate of Cu was unaffected by the soaking time, since Cu inside the wood is recovered after acid digestion of the wood samples. The fact that this is not the case strongly indicates that CuOx is precipitated in the solution. CuOx precipitated in the solution is not accounted for when recovery rates are estimated, since only the concentration in the solution is measured.

## Optimal duration of soaking prior to EDR

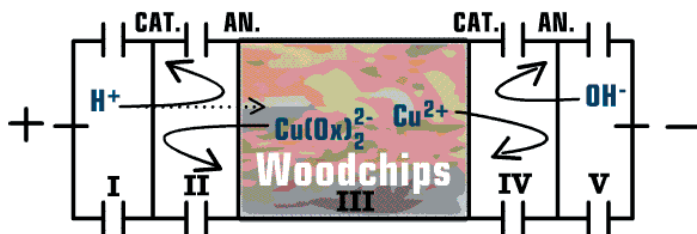
Based on these results it is presumed that the removal of neither Cu nor Cr is reduced with increasing soaking time. However, the removal efficiency declines after the initial 16-24 hours and since time is often an issue when the feasibility of a remediation method is considered, the optimum soaking time may be approximately 16 hours, but the wood may be soaked for a longer period of time for practical reasons without the remediation being influenced.

## 5.2 Current and voltage drop during EDR

When the EDR process was scaled up to pilot scale, it was observed that the removal of Cu and Cr from the aqueous phase in the middle compartment into the electrode compartments seemed slow and in some cases the amount of Cu and Cr found in the electrode compartments and in connection with the membranes after remediation was negligible. It was suggested that the current/voltage drop in the up scaled experiments may have been insufficient since it was limited by the available power supplies. In order to investigate the influence of the current on the removal of Cu and Cr from the middle compartment, a series of four experiments were conducted where the removal of Cu and Cr from the middle compartment was investigated at four different current densities.

### EDR setup

The EDR setup used differed from the setup presented in *section 4.1*. The setup is illustrated in figure 5. A smaller version of the EDR cell, with an internal diameter of 4 cm was used and the three-compartment setup from *section 4.1* was expanded to a five-compartment setup. The main reason for the extra compartments (compartment II and IV in figure 5) were to separate the electrodes from the removed ions from the middle compartment (compartment III). In a three compartment setup, the removed ions may react with the electrodes by precipitation /oxidation or reduction processes. Thereby the electric field may be influenced by precipitation onto the electrode. In a five compartment setup, the removed ions are trapped in collecting compartments placed in front of the electrode compartments by the use of ion exchange membranes and the transport of ions into the electrode compartment is negligible.



**Figure 5:** Five compartment EDR setup in principle. Compartment I & V: electrode compartments. Compartment II & IV: Collecting compartments. Compartment III: Middle compartment.

AN: Anion exchange membrane, CAT: Cation exchange membrane.

In the middle compartment no wood was present. Instead a middle compartment liquid from a pilot scale experiment was circulated. The removal of Cu and Cr was monitored by measuring the concentration of Cu and Cr in the middle compartment on an almost daily basis.

Experimental conditions

Four current densities were investigated: 0.4, 0.8, 1.6 and 4 mA/cm<sup>2</sup>. The experimental conditions for the experiments are presented in table 3 and only the current densities differed. The liquid that was circulated in the middle compartment came from the middle compartment of a pilot scale experiment after EDR where the wood had been soaked in 5% oxalic acid. The liquid had a concentration of approximately 22 ppm Cu and 65 ppm Cr. (See Christensen et al. 2004, exp. 2 for further information on the experiment).

Table 3: Experimental conditions for EDR of liquid.

Duration	7 days
Liquid in middle compartment	250 ml pilot scale middle compartment liquid*
Electrolytes (compartment I, II, IV, V)	250 ml 0,01 M NaNO3

\*liquid from pilot scale experiment 2 (see Christensen et al. 2004, exp. 2 for further information on the experiment)

During the experiments samples were taken from the middle compartment and the concentration of Cu and Cr was measured by AAS.

Results and discussion

In figure 6 the voltage drop are illustrated as a function of time at different current densities.

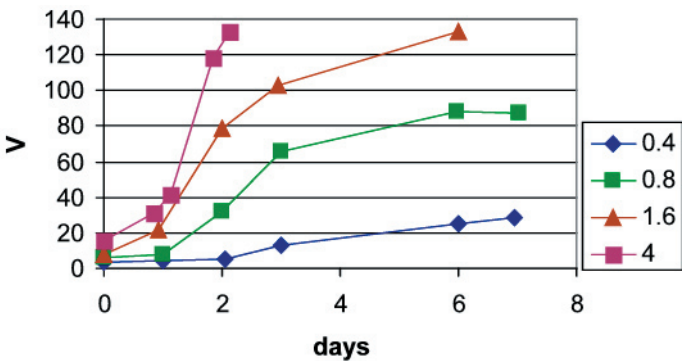
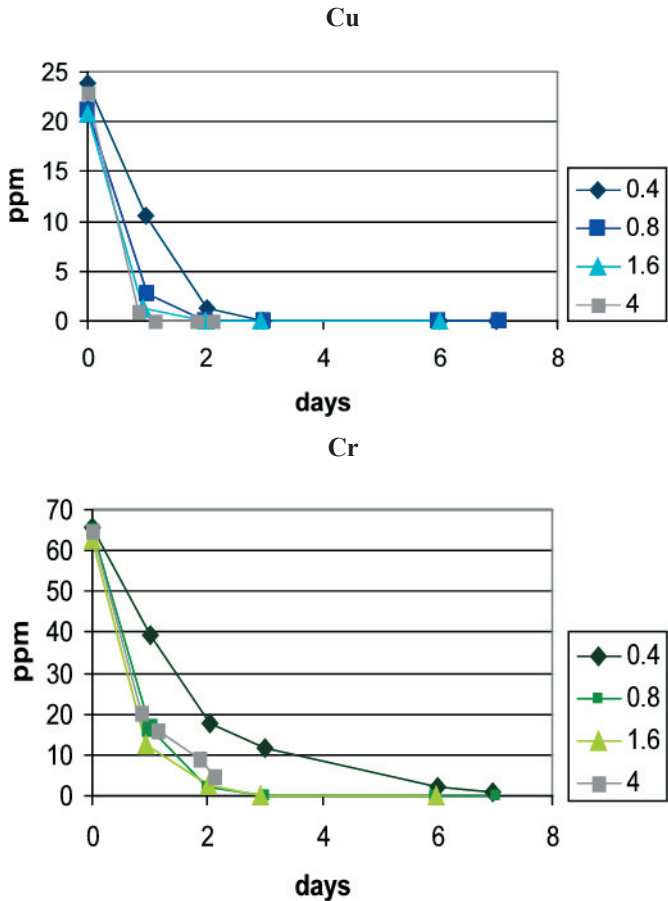


Figure 6: Voltage drop (V) as a function of time for four different current densities.

In all experiments the voltage increased with time. Since the current is kept constant, the increase in voltage may be regarded as increased electric resistance across the cell

with time. This is in agreement with the middle compartment being depleted of ions as they are removed by the electric field. In the experiments with the highest current densities (1.6 and 4 mA/cm<sup>2</sup>) the experiments were terminated ahead of time (after 6 and 2 days) since the voltage approached 133 V that is the upper limit of the power supply.

In figure 7 the concentration of Cu and Cr in the middle compartment as a function of time is presented.



**Figure 7:** The concentration of Cu and Cr in the middle compartment as a function of time for different current densities (mA/cm<sup>2</sup>)

After 2 days Cu could only be found in the middle compartment in the experiment with the lowest current density (0.4 mA/cm<sup>2</sup>). The concentration was very low (1.3 ppm) and after 3 days no copper was found here either. The removal rate of Cu was increased when the current density was increased from 0.4 to 0.8 mA/cm<sup>2</sup>. No additional effect could be seen when the current density was increased from 0.8 to 1.6 and 4 mA/cm<sup>2</sup>.



The same tendency were seen for Cr, however the removal of Cr was slower than Cu. In the experiment with the lowest current density, a low concentration of Cr (approximately 1 ppm) could still be measured in the middle compartment after 7 days. In the experiments with higher current densities of 0.8-4.0 mA/cm<sup>2</sup>, the removal rate of Cr was increased and similar in the three experiments. After 3 days Cr was removed in the experiments with current densities of 0.8 and 1.6 mA/cm<sup>2</sup>. In the experiment with the highest current density, Cr (4.5 ppm) was still found in the middle compartment at the time the experiment was terminated.

### Optimal current density considerations

Based on the series of experiments conducted here, the optimal current density when considering the removal of Cu and Cr from the middle compartment is between 0.4 and 0.8 mA/cm<sup>2</sup>. By increasing the current density further, no additional effect on the removal rates was obtained. This implies that the excess current was used to transport other ions than Cu and Cr. Probably protons and hydroxyl ions, as a consequence of water splitting. At the interface between the membrane and the solution, the concentration of electrolyte can approaches zero as the current is increased. When the current is increased still further, it will be carried in part by ions resulting from dissociation of water (*McRae 1988*).

The removal of especially Cr was hindered if the current density was increased from 1.6 to 4.0 mA/cm<sup>2</sup> due to high electric resistance and subsequently termination of the experiment.

In an EDR experiment the Cu and Cr has to move from the wood into the liquid before they can be removed from the middle compartment. This may very well be the rate determining step of the removal process, but was not taken into consideration here since no wood was present. How the actual presence of wood may influence the removal rate is not known. Based on the hypothesis that the faster the Cu and Cr are removed, the faster the remediation is complete; the current density should be closer to 0.8 mA/cm<sup>2</sup> than 0.4 mA/cm<sup>2</sup>. The current is however not selective of the target ions (Cu,Cr and As) but will also remove non target ions, including the oxalic acid ions. If oxalic ions are removed before complexes with Cu and Cr are formed, then the removal of Cu and Cr will probably decrease.

## 6. Summarising conclusions

The concentration of Cu, Cr and As in the wood may be measured by AAS after microwave assisted acid digestion of wood samples according to the programme presented in table 1. No additional Cu and Cr were released by adding H<sub>2</sub>O<sub>2</sub> during the digestion process. The L:S ratio in extraction experiments were set at 6:1 in order to match the L:S ratio during soaking of the wood prior to remediation (5.75:1).

The EDR setup and the experimental conditions regarding the carrying out of EDR

experiments were presented and apply to all experiments presented in this thesis unless other is mentioned. In experiments where the wood is soaked prior to the remediation, the optimum soaking period is estimated to approximately 16 hours, although this period may be increased for practical reasons without influencing the removal rate of Cu and Cr. The optimal current strength was found to be around  $0.8 \text{ mA/cm}^2$ . In an EDR cell with an inner diameter of 8 cm, this corresponds to a constant current of 40 mA.

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## 6 Electrodialytic remediation in laboratory scale: Identifying a suitable additive for removal of CCA from wood.

Identifying a suitable additive is one of the most important parameters to be investigated in the process of optimising the electrodialytic remediation method to removal of CCA from waste wood. In the following the main findings and development in order to optimise the remediation method with regards to suitable additives are presented. Only results from the laboratory experiments are presented here and they are described in a successive manner where new experiments are based on conclusions from earlier experiments.

All the experiments described below were done at acidic conditions. However it is important to mention a lot of the conducted experiments were rejected due to low removal of CCA. These experiments are not included here but the results include the attempt to remove CCA at alkaline pH, both by sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ ), ammonia ( $\text{NH}_3$ ) and ammonium oxalate ( $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ). The removal of Cu was 29-48% with the highest removal in experiments with  $\text{NH}_3$  as an additive but the removal of Cr at alkaline pH was less than 5% in every experiment conducted at alkaline pH – including experiments with sawdust.

Results from larger scale experiments are presented in paper form elsewhere in the present thesis (*Christensen et al 2004*).

### 1. Oxalic acid as an additive

The first additive to be tested was oxalic acid, since this was the additive used in electrodialytic remediation of sawdust (*Ribeiro et al. 2000*). In addition to that, others have used oxalic acid in extraction experiments (*Kazi & Cooper 1998 and Clausen 2000*) The reason oxalic acid has been tested so extensively can be attributed to observations of decay by brown rot fungi in wood that had been properly treated with Cr and Cu containing preservatives (*Stephan & Peek 1992*). Many brown rot fungi have a tendency to be potent producers of organic acids and oxalic acid in particular and these acids may detoxify the wood preservative, by forming complexes with the heavy metals in the wood preservative (*Eaton & Hale 1993*).

#### 1.1. Experimental conditions

In the first EDR experiment presented here a 5 cm long middle compartment was

used and the distance between the electrodes were approximately 10 cm. Wood chips from a pole (above ground) were used for this experiment. (see Chapter 4 for further information on the wood)

In table 1 the experimental conditions for the experiment are shown

**Table 1:** Experimental conditions for initial experiment with oxalic acid as additive

m wood	32.16 g
Duration	7 days
Additive	2.5 % oxalic acid
Anolyte	2.5 % oxalic acid
Catholyte	Saturated* oxalic acid
Current	40 mA

\* 100 g/L

## 1.2. Results and discussion

The distribution of Cu, Cr and As after remediation are presented in table 2. The results show that more than 90% Cu, and approximately 85% of both Cr and As were removed from the wood during the remediation. At the end of the experiment pH was approximately 1 in the electrolytes. Unfortunately pH was not measured in the middle compartment after remediation, but pH is expected to be in the same range as in the electrolytes due to the high concentration of oxalic acid.

**Table 2:** Distribution (%) of Cu, Cr and As after remediation

	Cu (%)	Cr (%)	As (%)
Wood	6	14	16
Catholyte	2	5	12
CAT	0	2	0
Anolyte	86	13	50
AN	4	61	1
Middle compartment	2	4	20

“Wood” refers to residual amount of metal in the wood. “CAT”: Cation exchange membrane, “AN”: Anion exchange membrane. Residual concentrations: Cu: 25 ppm, Cr: 135 ppm, As: 151 ppm

### Arsenic

A total of 83% of the initial As was removed, and the residual concentration in the wood was 151ppm

As seen in table 2, As is primarily moved towards the anode, but is also found in the liquid from the middle compartment and to some degree in the catholyte.

At pH 2, the dominating As(V) species is  $\text{H}_3\text{AsO}_4$ , but above pH 2.3  $\text{H}_2\text{AsO}_4^-$  dominates ( $\text{pK}_a = 2.3$  *Holtzclaw & Robinson 1988*). The fact that pH in this experiment is in the same range, makes it probable that these species will be dominating in the anolyte and middle compartment respectively. The dominating As(III) specie at pH 2 is  $\text{H}_3\text{AsO}_3$  ( $\text{pK}_a = 9.2$ , *Holtzclaw & Robinson 1988*). The fact that some As is found in the catholyte indicates that also cationic species may be present. According to *Ribeiro et al. (2000)* As(III) may exist as  $\text{AsO}^+$ ,  $\text{As}(\text{OH})^+$ , or in even more acid solutions  $\text{As}^{3+}$ , may exist and these species will move toward the cathode.

## Copper

A total of 94% of the initial Cu was removed during remediation and the remaining 6% resulted in a concentration of 25 ppm in the wood after remediation.

Almost all the removed Cu is found in the anolyte. This is in agreement with the fact that oxalic acid and Cu forms anionic species, most likely  $\text{Cu}(\text{Ox})_2^{2-}$ . ( $\beta_2 = 10^{9.21}$ , *Kotrly 1985*) The reason Cu dominates as  $\text{Cu}(\text{Ox})_2^{2-}$  instead of precipitated  $\text{CuOx}$  ( $K_{\text{sp}} = 4.43 \times 10^{-10}$ , *Chang 1992*) is attributed to the high concentration of oxalic acid in the compartments during remediation.

## Chromium

A total of 86% of the chromium was removed and the content of Cr in the wood afterwards was 135 ppm. Almost all chromium is removed in the direction of the anode and most of the chromium was at the end of the experiment found in connection with the anion exchange membrane. The anionic chromium species is probably  $\text{Cr}(\text{Ox})_3^{3-}$  ( $\beta_3 = 10^{10.51}$ , *Sillén & Martel 1971*). There is also a theoretical possibility that chromium(VI) is present as chromate or dichromate ( $\text{HCrO}_4^-$  or  $\text{Cr}_2\text{O}_7^{2-}$  in acidic solutions, *Cotton et al. 1987*), but since Cr(VI) is reduced to Cr(III) during the preservation, and given the fact that both wood and oxalic acid may react as a reducing agent and Cr(VI) is a strong oxidising agent in acid, the dominating anionic chromium specie is probably  $\text{Cr}(\text{Ox})_3^{3-}$ .

## 1.3. Conclusions and further work

In this experiment a total of 130 g oxalic acid (1.4 mol) was used to remediate 32.16 g wood chips. Good results were obtained, but it is not feasible to upscale a process where more than 4 ton of oxalic acid is needed to remediate 1 ton of waste wood. Instead a new procedure is introduced, where the wood is soaked prior to the EDR.

## 2. Soaking of wood in oxalic acid prior to remediation

By introducing soaking, an additional step is introduced into the remediation process. The dry wood is placed outside the EDR cell and soaked in a solution of the desired additive (e.g. oxalic acid). A higher concentration of the chemical is used when the

chemical is introduced during soaking compared to during EDR. After minimum 16 hours the wood is removed from the soaking solution and placed in the middle compartment of the EDR cell. During EDR, water is used in the middle compartment and 0.01 M  $\text{NaNO}_3$  is circulated in the electrode compartments. The total amount of chemical (oxalic acid) to be used for the remediation is reduced.

## 2.1. Expected advantages by soaking

The soaking is expected to serve multiple purposes:

- ▶ **Reducing the total cost of the process by reducing the amount of chemical.** The L:S ratio when soaking wood is less than 6 in the laboratory. Meaning 300 kg oxalic acid to 1 ton wood when the wood is soaked in a 5% oxalic acid solution.
- ▶ **Optimising the current efficiency by reducing the number of ions in the middle compartment during EDR.** The amount of oxalic acid ions in the middle compartment will be limited to what the wood chips have taken up during soaking. Some of the oxalic acid will move from the wood into the water in the middle compartment during EDR, but the amount of current being wasted on removing free oxalic ions will be greatly reduced compared to the situation where oxalic acid is used in the middle compartment. Also the possibility of the oxalic acid forming complexes with the CCA in the wood, before the oxalic acid is removed by the electric current is improved by soaking. In addition to reducing the amount of excess oxalic acid ions (non target ions), the amount of Cu, Cr and As to be removed during EDR is reduced since a portion of CCA is removed by extraction during soaking.
- ▶ **Improving the work environment.** When the handling of harmful chemicals (oxalic acid etc.) is reduced and also restricted to a limited period before EDR, as opposed to using potential harmful chemicals in larger quantities and during the whole EDR period, then the work environment must be considered improved for the workers that administer the experiments.
- ▶ **Possibility of reusing the soaking solution.** Besides the financial benefits that would come from reusing the additive, the advantages would be that a smaller amount of soaking solution with a larger concentration of Cu, Cr and As would be generated. This would make the handling of the liquids easier and the possible recovering of the metals more beneficial.

In the following the possibility of reusing a soaking solution of 5% oxalic acid is addressed.

## 2.2. Reuse of oxalic acid soaking solution:

The possibility of reusing the soaking solution was investigated. When wood is soaked in oxalic acid the uptake is generally just below 1L oxalic acid to 1L wood (with a wood density of 0.5 kg/L). However, the fact that one litre wood takes up much more

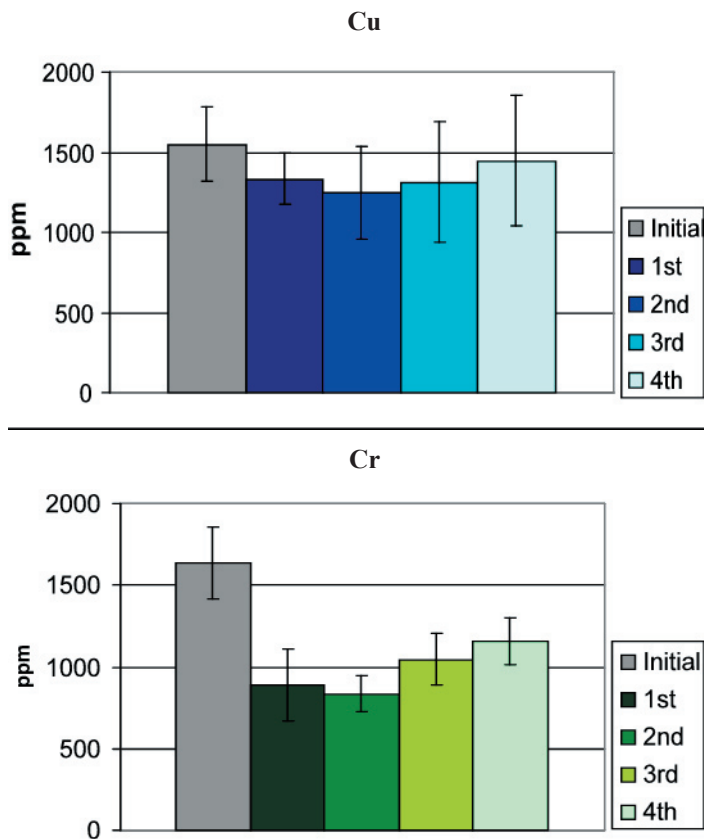
space when in the form of wood chips, makes it necessary to use substantially more oxalic acid for soaking than the wood is able to take up. The L:S ratio used during soaking is 5.75:1, corresponding to approximately 3 L oxalic acid to 1 L wood. This makes it interesting to investigate the possibility of reusing the soaking solution

Experimental conditions

An experiment were made where the soaking solution was used and reused a total of four times. 20 g wood chips (pole, below ground) were soaked in 115 ml 5% oxalic acid (L:S 5.75). After 24 hours of soaking, the wood was removed and approximately 40-50 ml. fresh 5% oxalic acid was added to obtain the initial volume of 115 ml soaking solution. A new batch of 20 g wood chips was added and the soaking process was repeated. Four bathes of wood were soaked altogether.

Results and discussion

The concentration of Cu and Cr was measured in the wood chips after soaking and the results are shown in figure 1.



**Figure 1:** Concentration of Cu and Cr in wood after soaking in 5% oxalic acid. Mean value of five measurements ± 95% CL. Soaking solution used a total of four times.



When comparing the concentration of Cu and Cr in the wood with the number of times the soaking solution has been used there seems to be a slight increase in the concentration when the soaking solution is used for the 3rd and 4th time, but based on the 95% confidence limits, this increase is not statistically significant. For Cu the variation is high (large confidence interval) both in the initial wood and after soaking. Based on these results it was concluded that the soaking solution of 5% oxalic acid could be used a total of four times.

The actual reuse of soaking solutions occurred only in the larger scale experiments and the solutions were never used more than a total of three times.

### 2.3. EDR results with initial soaking in oxalic acid

In chapter 5 a series of EDR experiments were presented in order to identify the optimal soaking time. It was found to be close to 16 hours but the wood could be soaked longer for practical reasons without influence on the remediation.

Here the remediation of Cu and Cr after 16 hours soaking is presented. Experimental conditions for the experiments can be seen in *chapter 5*.

In table 3 the distribution of Cu and Cr after remediation are presented.

**Table 3:** Distribution of Cu and Cr after remediation (16 hours soaking in 5% oxalic acid)

	Cu (%)	Cr (%)
Wood	39	14
Cathode side*	5	2
Anode side*	39	31
Middle compartment	3	2
soaking	13	52

\*Side refers to total amount of metal in: electrolyte, membrane and electrode  
Wood refers to residual amount of metal in the wood.

A total of 61% Cu and 86% Cr were removed after EDR giving average residual concentrations of 632 ppm Cu and 251 ppm Cr. The introducing of soaking meant that 13% Cu and 52% Cr was removed without the use of current. The part of Cu and Cr that was removed during EDR showed similar distribution as when no soaking was used Cu and Cr was primarily removed towards the anode side, probably as anionic complexes with oxalate ( $\text{Cu}(\text{Ox})_2^{2-}$  and  $\text{Cr}(\text{Ox})_3^{3-}$ ) *see section 1.2*.

### 2.4. Conclusions and further work

By introducing soaking prior to EDR it appears that a variety of both practical and financial advantages can be obtained. The removal of Cr seems relatively unaffected by the introduction of soaking, and more than 50% of the initial Cr in the wood was removed during soaking. However oxalic acid seems to be a poorer choice as additive when the removal of Cu is considered. Only 61% of Cu was removed in total when

oxalic acid is used to soak the wood.  
An alternative additive suitable for the removal of both Cu and Cr must be found.

### 3. Extraction experiments with new additives

A series of extraction experiments were made with different acids and combinations of acids.  
Phosphoric acid, citric acid and tartaric acid were tested in different combinations and in some combinations oxalic acid was included.  
Phosphoric acid had earlier proven effective in the removal of especially Cu from wood impregnated with Cu and Cr (*Christensen 2000*). Citric acid had shown potential in removal of heavy metals from fly ash (*Pedersen 2002*) Tartaric acid was included because of the similar structure to citric acid. Tartaric acid is smaller than citric acid and has one less carboxylic acid unit.

#### 3.1. Experimental conditions

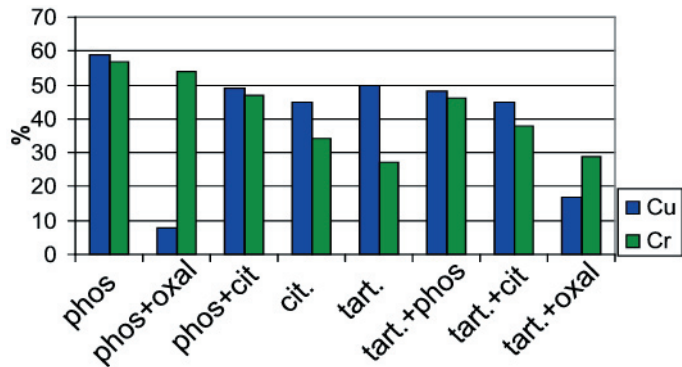
(see table 4). Each extraction experiment consisted of 5 gram wood (pole below ground) and 30 ml acid according to table 4 that were mixed and placed on a shaking cupboard for 24 hours. pH was measured after 10 min. and again after 24 hours, before the samples were filtrated. The pH did not change during the 24 hour period.

**Table 4:** Acids and combination of acids used for extraction of Cu and Cr from wood chips

Acid	Final pH
0,5 M Phosphoric acid (phos)	1.1
0,5 M Phos + 2,5% oxalic acid	0.7
0,5 M phos + 0,5 M citric acid	1.3
0,5 M citric acid	1.7
0,5 M tartaric acid (tart)	1.9
0,5 M tart + 0,5 M phos	1.4
0,5 M tart + 0,5 M citric acid	1.8
0,5 M tart + 2,5% oxalic acid	2.0

#### 3.2. Results and discussion

In figure 2 the amount of Cu and Cr removed during the extraction are shown. The results are based on the measured concentration in the liquid compared to the initial content of the metal in the wood. The concentration of Cu and Cr in the wood was not measured.



**Figure 2:** Removed (%) of initial Cu and Cr after 24 hours extraction, . Plotted as mean values, based on duplicates. L:S = 6, See table 4 for details on acids.

Phosphoric acid seems to be a suitable additive for the removal of both Cu and Cr. Oxalic acid is not suited for the removal of Cu even when it is mixed with other acids. When phosphoric acid is mixed with oxalic acid, the removal of Cu is restricted. Only 8% Cu can be extracted when the two acids are combined, whereas 60% Cu can be extracted when only phosphoric acid is used. The same pattern is seen when comparing tartaric acid to a combination of tartaric and oxalic acid.

The extraction of Cr is not affected by oxalic acid, but at the same time no additional Cr can be extracted when two acids are combined. Of the additives tested here the highest removal of both Cu and Cr were obtained with phosphoric acid and the combinations of phosphoric/citric acid, and phosphoric/tartaric acid.

### 3.3. Conclusions and further work

Based on the extraction experiments phosphoric acid seems to be a suitable soaking additive for both Cu and Cr and phosphoric acid in combination with citric acid or tartaric acid also shows promising. In order to evaluate the usefulness of these additives for EDR, a series of EDR experiments were made.

## 4. EDR experiments with new additives

To evaluate phosphoric and citric acid as additives, a total of five EDR experiments were made with different concentrations of the two acids to be used as soaking solutions.

## 4.1. Experimental conditions

The five different combinations of soaking solution additives were:

- 0.1 M phosphoric acid
- 0.5 M phosphoric acid
- 0.1 M phosphoric, 0.1 M citric acid
- 0.1 M phosphoric, 0.5 M citric acid
- 0.5 M phosphoric, 0.5 M citric acid

In table 5 the experimental conditions are presented. The wood was fine fraction of mixed wood and was soaked for 19 hours (L:S 5.75)

**Table 5:** Experimental conditions for EDR experiments with phosphoric and citric acid

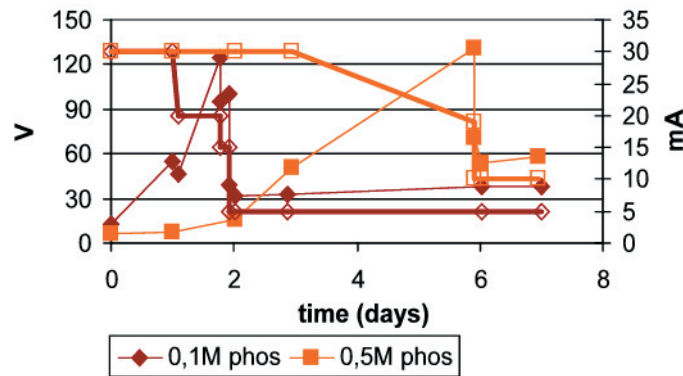
m wood	70 g
Duration	7 days
Middle compartment	Water
Anolyte	0.01 M NaNO <sub>3</sub>
Catholyte	0.01 M NaNO <sub>3</sub>
Current	*30 mA

\*Initial current. In all experiments the current was reduced during the exp. See text and Figure 3 and 4 for further details.

## 4.2. Results and discussion

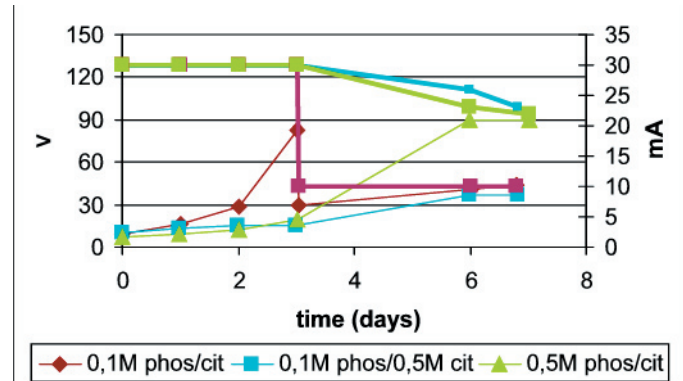
### Current and voltage drop

It was not possible to maintain the current at 30 mA during the experiments. The current and voltage drop for the experiments with phosphoric acid alone are illustrated in figure 3. In the experiments with 0.1 M phosphoric acid, the current had to be reduced to 5 mA after 2 days, as the voltage reached maximum for the power supply. The current was maintained at 30 mA for a longer period when 0.5M phosphoric acid was used. In this experiment the current was reduced to 10 mA for the last 24 hours of the experiment. The main reason for the high resistance is most likely lack of ions in the middle compartment and therefore the effect is most pronounced when 0.1 M phosphoric acid is used.



**Figure 3:** Voltage drop (thin lines) and current (thick lines) as a function of time for experiments where phosphoric acid was used for soaking.

When a combination of phosphoric and citric acid is used, there is a larger amount of ions (charge) compared to phosphoric acid alone. This is in agreement with the observed voltage drop and current (see figure 4).



**Figure 4:** Voltage drop (thin lines) and current (thick lines) as a function of time for experiments where combinations of phosphoric and citric acid was used for soaking.

When a combination of 0.1M phosphoric and citric acid was used as soaking solution, the current strength was reduced to 10 mA after 3 days as a precaution because of the increasing voltage drop. The voltage increase was dramatic from day 2 to day 3 and there was a concern that the voltage would increase even further. Since day 3 was a Friday and the experiment was not inspected during the weekend it was decided to reduce the current in order to prevent the voltage from reaching maximum during the weekend. The resistance (and subsequently the voltage drop) was never as high as when phosphoric acid was used alone. When a higher concentration was used, the voltage drop did not exceed 90 V, but the current was reduced never the less. This was

due to an operational error that resulted in the voltage drop being limited to 90 V and 36 V in the two experiments. When the voltage drop was restricted, the current was automatically reduced. Especially when 0.5 M phosphoric/citric acid was used, the current could probably have been maintained at 30 mA if the power supply had been correctly set.

### Removal of Cu and Cr

In table 6 the percentage Cu and Cr that was left in the wood and the residual concentrations after remediation is compared to the total charge consumption in the experiments.

Additive	Cu in wood		Cr in wood		Charge consumption (C)
	%	ppm	%	ppm	
0.1 M phosphoric acid	35%	450 ppm	85%	1130 ppm	6402
0.5 M phosphoric acid	13%	165 ppm	57%	751 ppm	14815
0.1 M phosphoric acid + 0.1 M citric acid	23%	294 ppm	68%	908 ppm	11106
0.1 M phosphoric acid + 0.5 M citric acid	14%	174 ppm	37%	499 ppm	16746
0.5 M phosphoric acid + 0.5 M citric acid	15%	187 ppm	51%	685 ppm	16614

**Table 6:** percentage and concentration of Cu and Cr in the wood after remediation with different soaking solution additives. Total charge consumption (C) for the EDR experiments is presented in the last column.

When phosphoric acid is used alone, the remediation of both metals is improved when the concentration is increased from 0.1 M to 0.5 M. The removal of Cu was most efficient and only 13% is left in the wood after remediation, compared to 57% chromium. When combining phosphoric and citric acid the remediation of Cr is improved. 37% Cr is left in wood when a combination of 0.1 M phosphoric and 0.5 M citric acid is used as an additive for soaking. The remediation of Cu and Cr are improved when the concentration of citric acid is increased from 0.1 M to 0.5 M. By increasing the concentration of both acids to 0.5 M, the remediation is reduced for Cr and unchanged for Cu. The lack of removal may be caused by increased competition between especially Cr and the higher concentration of additive ions (non target ions).

### 4.3. Conclusions and further work

Based on EDR results a soaking solution of 0.1 M phosphoric acid and 0.5 M citric acid is most suitable of the five acid combinations for remediation of both Cu and Cr. This combination was later evaluated in a bench scale experiment with 12 kg wood chips. Here 15% Cu, 33% Cr and less than 15% As was left in the wood after remediation, corresponding to concentrations of 145 ppm Cu, 436 ppm Cr and less than 100 ppm As in the wood after remediation (*Ottosen & Kristensen 2002*).

The removal of Cr was not improved when oxalic acid was replaced by phosphoric acid or a combination of phosphoric and citric acid. However the removal of Cu was greatly improved when oxalic acid was replaced by phosphoric acid. A combination of the two acids seemed to inhibit the removal of Cu dramatically (see figure 2). Only 8% of the initial Cu could be found in the liquid after extraction.

Instead of mixing phosphoric acid and oxalic acid it was decided to investigate the effect of soaking the wood in one acid first and afterwards in the other acid, a process that was named: dual soaking.

## 5. Dual soaking (order of)

The fact that the removal of Cu was inhibited when the phosphoric and oxalic acid were combined (see figure 2) indicates that the order of the soaking may be important. A soaking experiment was made where the order of soaking was investigated.

### 5.1. Experimental conditions

20 g wood chips (mixed wood, fine fraction) was soaked in 115 ml 5% oxalic acid for 24 hours. Then the wood was removed and soaked in 115 ml 0.5 M phosphoric acid for 70 hours (over the weekend). In another experiment the order of soaking was reversed. Both experiments were done in duplicates.

### 5.2. Results and discussion

In table 7 the concentration of Cu and Cr in the wood, as well as the percent Cu and Cr left in the wood, after dual soaking is presented.

Order of soaking	[Cu] ppm	%Cu of initial	[Cr] ppm	%Cr of initial
1. Oxalic, 2. phosphoric	641	50%	275	21%
1. Phosphoric, 2. oxalic	223	17%	471	35%

**Table 7:** Cu and Cr in the wood after dual soaking in 5% oxalic acid and 0.5M phosphoric acid. Initial concentrations: Cu:1279 ppm, Cr:1334 ppm.



It seems that both the removal of Cu and Cr are influenced by the order of soaking, but whereas more Cu is removed when the wood is soaked in phosphoric acid before oxalic acid, the opposite is the case for Cr. When the order of soaking is phosphoric acid followed by oxalic acid the concentration of Cu is reduced by 400 ppm compared to the concentration when the order of soaking is reversed. The removal of Cr is highest when the wood is soaked in oxalic acid before phosphoric and the concentration of Cr is reduced by 200 ppm compared to the reverse order of soaking. When using dual soaking it seems that soaking in phosphoric acid before oxalic acid, is the order that has the overall best removal of Cu and Cr.

A possible explanation to the difference in effect of soaking order on the two metals may be precipitation during soaking. The initial soaking is presumed to be most important, since the concentration and availability of the metals are higher in the first soaking compared to the second. CuOx has a limited solubility ( $K_{sp} = 4.43 \times 10^{-10}$ , *Chang 1992*) and is therefore most affected (inhibited) by soaking in oxalic acid. For Cr the removal is highest when oxalic acid is used first, probably as a consequence of oxalic acid being more suited to the removal of Cr than phosphoric acid. The wood may not take up the second additive to the same degree as the first, since the wood is already saturated with the first additive and therefore oxalic acid may not remove the same amount of Cr when it is used as the second additive.

### 5.3. Conclusions and further work

Both the removal of Cu and Cr were affected by the order of soaking, unfortunately the effect was opposite for the two metals. Phosphoric acid followed by oxalic acid favoured the removal of Cu, however the opposite order of soaking increased the removal of Cr – but decreased the removal of Cu. Since the largest influence was on the removal of Cu, the soaking in phosphoric acid before oxalic acid seems to be the order that has the overall best removal of Cu and Cr.

To investigate the overall removal efficiency by the dual soaking a EDR experiment was done.

## 6. Dual soaking followed by EDR

An EDR experiment was carried out with dual soaking in phosphoric acid, followed by oxalic acid.

### 6.1. Experimental conditions

In the experiment the wood (mixed wood, fine fraction) was soaked in 0.5 M phosphoric acid prior to soaking in 5% oxalic acid. The duration of each soaking was 18 hours. The experimental conditions can be seen in table 8.

Table 8: Experimental conditions for EDR after dual soaking

m wood	70 g
Duration	7 days
Middle compartment	Water
Anolyte	0,01 M NaNO3
Catholyte	0,01 M NaNO3
Current	30 mA

## 6.2. Results and discussion

After EDR 92% Cu and 83% Cr was removed from the wood. In table 9 the concentration of Cu and Cr are compared to the initial concentrations.

**Table 9:** Concentration of Cu and Cr in wood before and after remediation (dual soaking + EDR)

	[Cu]ppm $\pm 95\%$ CL	[Cr]ppm $\pm 95\%$ CL
Initial	1279 $\pm$ 66	1334 $\pm$ 91
After EDR	102 $\pm$ 15	232 $\pm$ 42

In figure 5 the distribution after remediation is shown. The majority of both Cu and Cr were removed during soaking. In total 85% of Cu was removed during soaking and in the first soaking alone, 69% was removed.

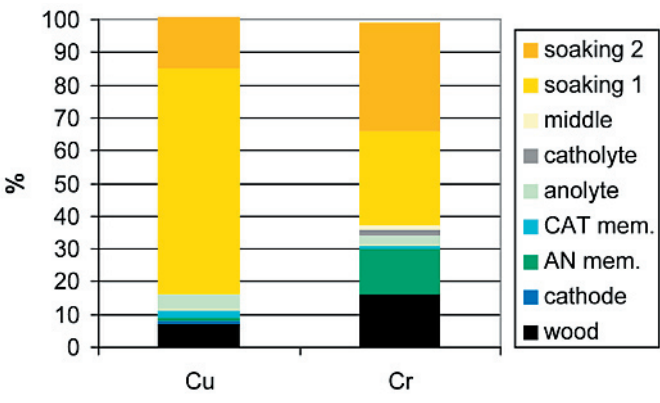


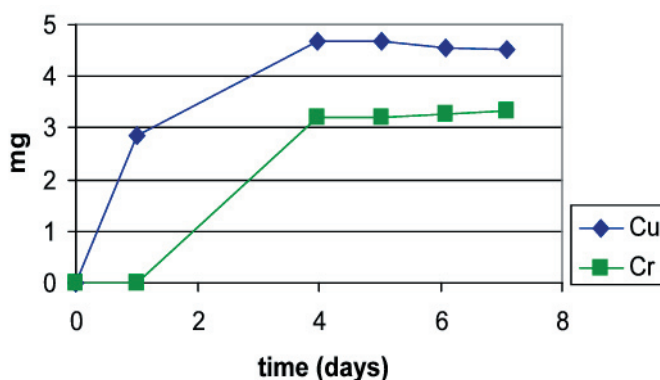
Figure 5: Distribution of Cu and Cr after remediation with dual soaking. Soaking 1: phosphoric acid, soaking 2: oxalic acid

The remaining part of the removed Cu was primarily removed towards the anode side. At the end of the remediation 5% of the Cu was located in the anolyte. No Cu was found in the middle compartment (liquid) at the end of the experiment.

For Cr the removal was similar in both soakings. 29% was removed during soaking in phosphoric acid and 33% was removed in oxalic acid. At the end of the EDR experiment 17% was removed towards the anode side with 14% found in connection with the anion exchange membrane and 3% in the anolyte. Only 1% Cr was found in the middle compartment (liquid) after remediation.

The removal of Cu and Cr towards the anode side is in agreement with the finding in earlier experiments with oxalic acid (chapter 1.2 & 2.3) and is presumed to be due to anionic oxalate complexes of both Cu and Cr. The reason Cr unlike Cu, is found predominantly in connection with the anion exchange membrane and to a lesser degree in the anolyte is also in agreement with earlier findings and may be due to the size of the chromium oxalate species and/or the fact that chromium is trivalent and Cu is divalent.

In figure 6 the amount of Cu and Cr in the anolyte is illustrated as a function of time. It is seen that the removal took place within the first four days of the experiment. This suggests that the removal of Cu and Cr will not be increased simply by prolonging the duration of the experiment.



**Figure 6:** Amount o(mg) of Cu and Cr located in the anolyte as a function of time.

## 7. Summarising conclusions on the process of identifying a suitable additive

The work of optimising the EDR process has mainly been focused on finding a suitable additive to facilitate the mobilisation and removal of Cu and Cr under acidic conditions. Initially oxalic acid was used, first directly in the middle compartment during EDR and later as soaking solution prior to EDR. The switch to soaking solution was in part an attempt to reduce the amount of chemical to be used in the EDR process. However the removal of especially Cu was reduced with the reduction of the

amount of oxalic acid. It seems that the concentration of oxalic acid was reduced so precipitates of CuOx gained more influence compared to the  $\text{Cu}(\text{Ox})_2^{2-}$  species that was formed in the excess of oxalic acid.

Since the high concentration of oxalic acid was not realistic in a larger scale remediation, the search for a new additive began. The most promising additives when a single soaking was used, was phosphoric acid and a combination of phosphoric and citric acid.

In the laboratory it was found that phosphoric acid was a suitable additive for Cu but not so effective for Cr. The opposite was the case when oxalic acid was used for soaking, here Cr could be removed, but Cu was not removed to the same degree. Based on this it was decided to do an EDR experiment with the two acids. Extraction experiments had shown that by mixing the two acids, the removal of Cu was greatly inhibited and it was therefore decided to introduce dual soaking. The optimum order of soaking was found to be phosphoric acid followed by oxalic acid. After dual soaking and EDR only 8% of the initial Cu was left in the wood and 17% of the Cr. This corresponds to concentrations of 102 ppm Cu and 232 ppm Cr left in the wood. This was the best result obtained in the laboratory when soaking was used. The profiles of Cu and Cr in the analyte as a function of time indicate that the remediation could not be optimised further by simply increasing the duration of the experiment.

The remediation in larger scale as described elsewhere (*Christensen et al. 2004*) are based on the finding in the laboratory.

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# Electrodialytic Remediation of CCA-Treated Wood in a 2 Cubic Metre Pilot Plant

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## Abstract

A pilot plant for electrodialytic remediation of up to 2 m<sup>3</sup> wood treated with chromated-copper-arsenate (CCA) has been designed and tested at the Technical University of Denmark. Several process parameters were investigated, and it was found that the use of collecting units and soaking of the wood prior to the electrodialytic process had a positive influence on the remediation process. There was a tendency towards easier remediation of wood chips < 2cm, than larger wood size fractions. The influence of the electrode distance could not be fully investigated due to the experimental setup but it is expected that the use of collecting units will keep any influence to a minimum. The best remediation efficiency was obtained in an experiment with an electrode distance of 60 cm, and 100 kg wood chips. In this experiment 87% copper, 81% chromium and >95% arsenic was removed. The corresponding final concentrations in the wood were 163 ppm Cu, 252 ppm Cr and less than 43 ppm As. Only one other experiment was analysed for arsenic and here 95% was removed. The electrode distance was 1.5 m and the results indicate that arsenic may be the easiest removable of the copper, chromium and arsenic investigated here. This is very encouraging since arsenic is the CCA component of most environmental concern.

## Keywords

CCA-treated waste wood, electrodialytic remediation, oxalic acid, phosphoric acid, pilot plant

# 1. Introduction

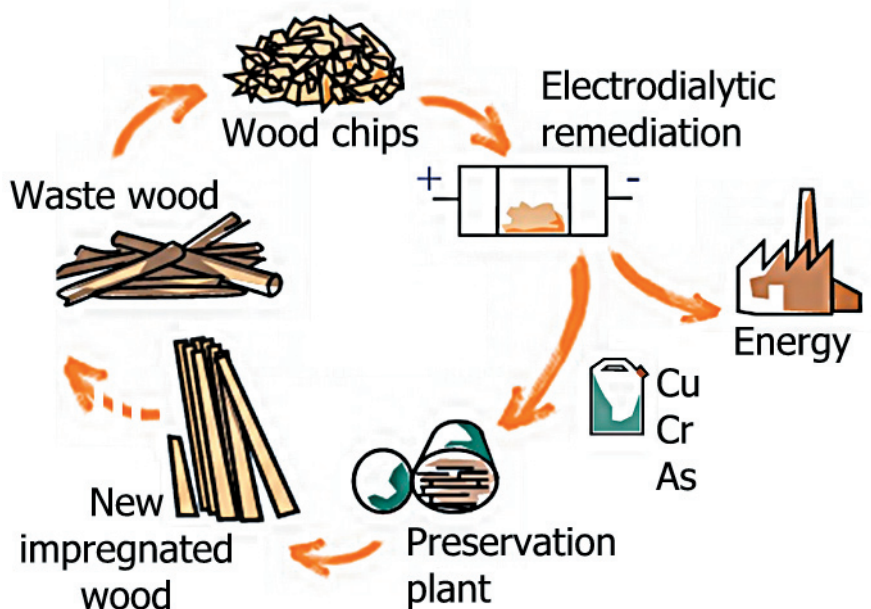
## 1.1 CCA-treated waste wood

The service life of wood treated with Chromated Copper Arsenate (CCA) may be 20-50 years or even more [1] implying strong fixation of the CCA and subsequently low leaching from wood while in service. Low leaching also means that a large proportion of the CCA is still present in the wood when it is removed from service. Cooper et al. [2] found CCA retentions well above the toxic threshold for decay in poles removed from service after 1-50 years.

The average life span for residential lumber is often much shorter, in part because aesthetic reasons also play a role in determining the service life. In a survey conducted by McQueen & Stevens [3] the disposal of residential decks made with CCA-treated lumber was reported and approximately 30% of the decks were disposed for aesthetic reasons. The average service life for these decks was 7 years.

Low leaching of CCA and disposal for aesthetic reasons means that the wood still contains high amounts of CCA when it becomes waste wood.

The amount of treated waste wood is increasing in the present years and it is estimated that in Denmark alone the amount of treated waste wood to be disposed will increase from 17,000 tons in 1992 to 100,000 tons in 2010 [4]. Similar trends are seen in the rest of the world. In Canada the volume of CCA treated wood to be removed from service is expected grow substantially in the next 10 years and stabilize at a level of close to 2 million cubic metres per year [1] and in Germany and France the total amount of wood waste is around 3-4 million tons per year of which more than 2 million tons are characterised as dangerous [5]. The large amount of wood and the high content of copper (Cu), chromium (Cr) and arsenic (As) from the CCA make an environmental safe handling method for the wood desirable. Incineration of CCA-treated wood is not allowed in Denmark. This is primarily due to arsenic release to the atmosphere, and the fact that the heavy metals will be concentrated in the combustion residues [4].



**Figure 1:** Proposed life cycle for CCA treated wood

In figure 1 a proposed life cycle for CCA-treated wood is presented. The CCA treated waste wood is chipped and the Cu, Cr and As are removed by electro-dialytic remediation. Afterwards the wood may be burned, thereby utilizing the energy resource of the wood. To be able to use the wood as a bio fuel, the removal of Cu, Cr and As has to be 100%, but if the As is removed and the concentration of Cr and Cu is reduced, then the wood may be burned in a municipal solid waste incinerator (MSWI). The removed Cu, Cr and As may be used for the production of new CCA, but since the use of CCA is being restricted in most of the world, the metals may be used in other parts of the industry instead, or stabilized for safe disposal.

## 1.2 Electrodialytic remediation (EDR)

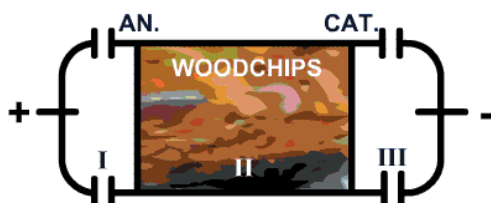
Electrodialytic remediation is a method developed and patented at the Technical University of Denmark (DTU). Initially the method was developed for removing heavy metals from polluted soil [6] [7]. The method uses a direct electric current as a cleaning agent and combines it with the use of ion exchange membranes to separate the electrolytes from the soil. Good results have been obtained, and subsequently the method has been tested on a wider range of materials including fly ash, sludge, harbour sediments and impregnated waste wood [8] [9] [10] [11] [12].

In laboratory scale experiments CCA-treated waste wood has been remediated both as sawdust and wood chips with encouraging results. In sawdust approximately 95% Cu, 90% Cr and more than 96% As has been removed [11] and in remediation of wood chips, removal results of more than 90% Cu and approximately 85% of both

Cr and As has been obtained [13].

Based on the good results obtained in the laboratory, the upscaling of the electrodia-lytic remediation has now been tested. In the experiments presented here, between 94 kg and 469 kg wood chips was used in each experiment, compared to the 50-70 grams used for experiments in laboratory scale.

A schematic presentation of an electrodia-lytic cell is shown in figure 2.



**Figure 2:** Schematic presentation of an electrodia-lytic cell. Compartment I and III is the anode and cathode compartment respectively, the wood chips are placed in compartment II.

AN: Anion exchange membrane, CAT: Cation exchange membrane

The laboratory cell consists of three compartments: an anode compartment (I), a cathode compartment (III) and a middle compartment (II) containing the wood chips (figure 2). The catholyte is separated from the middle compartment by a cation ex- change membrane, a membrane that only allows positive ions – cations - to pass. The anolyte is separated from the middle compartment by an anion exchange membrane, a membrane that only allows negative ions – anions- to pass.

When an electric potential is applied to the electrodes, the current in the cell will be carried by ions in the solutions. Accordingly cationic species will migrate towards the cathode and anionic species will migrate towards the anode. With ion exchange mem- branes placed as described above, no current carrying ions can pass from the electrode compartments into the middle compartment, while ions can be transported from the middle compartment into the electrode compartments. In this system the current is thus prevented from carrying highly mobile ions from one electrode compartment through the middle compartment into the other electrode compartment. Furthermore competition between such highly mobile ions from the electrode compartments and the ions in the middle compartment is avoided. The electrodia-lytic remediation method is described in further details in [7] [14].

## 2. Experimental section

### 2.1 Wood

The wood used in the present experiments was supplied by RGS90, the largest recycling company in Denmark. From a large pile of demolition wood waste approxi-

mately 10 m<sup>3</sup> of impregnated wood was collected. By visual inspection it can be very difficult to see if old (weathered) wood is impregnated or not, therefore Chromazurol S, a colour reagent turning blue in contact with Cu was used to identify the impregnated wood. After sorting, the wood was chipped and divided into three size fractions (< 2 cm, 2-4 cm and > 4 cm) by sieving. In table 1 the mean concentration of Cu, Cr and As in the wood is given.

**Table 1** Mean Concentration  $\pm 95\%$  CL of Cu, Cr and As in Waste Wood. Mean values are based on 179 samples for Cu and Cr and 95 samples for As.

	ppm (mg/ kg wood)
[Cu]	1279 $\pm$ 66
[Cr]	1334 $\pm$ 91
[As]	837 $\pm$ 114

2.2 Analytical Methods

Atomic Absorption Spectroscopy (AAS) in flame was used for measuring concentrations of Cu, Cr and As. Wood samples were analysed after microwave assisted acid digestion (0.4 g wood to 10 ml nitric acid) and dilution to a final volume of 25.0 ml. Aqueous samples (electrolytes etc.) were preserved with nitric acid (1:4) prior to AAS.

The concentration of As had to be measured at an external laboratory and therefore only selected samples were measured for As in the present investigation.

2.3. Pilot plant



**Figure 3:** The pilot plant in use. Wood chips in yellow plastic nets are placed between collecting units, where the Cu, Cr and As from the wood is collected. The end units contains the electrodes, and are named electrode units.

A pilot plant has been designed for the remediation of up to 2 m<sup>3</sup> treated wood waste. Figure 3 shows the pilot plant in use. It consists of a box, approximately 3 meter long, 1 meter wide and 1 meter high. Inside the box, there are ribs for every 35 cm and at these ribs it is possible to place a collecting unit or an electrode unit (electrode compartment). When the full capacity of the plant is in use, the electrode units are placed in each end of the box, thereby giving a distance between the electrodes of 3 meters. The electrode units may also be placed at the ribs, thereby allowing the distance between the electrodes to vary from 30 cm to 3 meters. The pilot plant was in principle only an upscale of the laboratory set up, but some adjustments was made in the up scaling. Due to the larger size, the distance between the electrode units (where the ions are collected in laboratory scale experiments) may become a limiting factor on the remediation time or efficiency. To compensate for this, collecting units were introduced. Collecting units were placed between the electrode units and had a cations exchange membrane on one side and an anion exchange membrane on the other side. The membranes make it possible to trap the ions inside the units. By introducing the collecting units, the distance the ions have to travel before being captured could be reduced to 30 cm. The amount of wood to be treated may vary between approximately 300 L and 2 m<sup>3</sup>.

## 2.4 Remediation Experiments

A total of seven pilot plant remediation experiments are presented here, and in table 2 the experimental conditions for the experiments are outlined.

In all experiments but exp. 4, the wood was soaked in an additive before remediation. The wood was soaked in large open containers. The L:S ratio (additive:wood) was 4:1 in every soaking. After soaking the wood was placed in the pilot plant and covered with tap water and the current was applied. In the electrode units and collecting units approximately 20 l 0.01 M NaNO<sup>3</sup> was circulated. During the remediation, the pH was adjusted with nitric acid to maintain pH 2 in the units to prevent precipitation. After remediation the distribution of Cu and Cr was measured in all seven experiments. The content of Cu and Cr was measured in the soaking solutions, the units, in the middle compartments and in the wood. The distribution of As was only measured in exp. 3 and exp. 6 due to the fact that the analysis had to be made at an external laboratory and at high costs.

Experiment 1 and 2 differed in the use of collecting unit. By comparing these experiments the utility of collecting units on the remediation could be evaluated. In experiment 3 the additive in the soaking solution was changed from oxalic acid to a dual soaking sequence of phosphoric acid followed by oxalic acid. By comparing experiment 1 with experiment 3, the additives could be evaluated, however the duration of the experiments needs to be taken into consideration, since experiment 3 lasted almost twice the time experiment 1 did. In experiment 4 the wood was not soaked before remediation, and instead oxalic acid was used as an additive during the remediation. Experiment 4 could be compared to experiment 1 for an evaluation of oxalic acid as

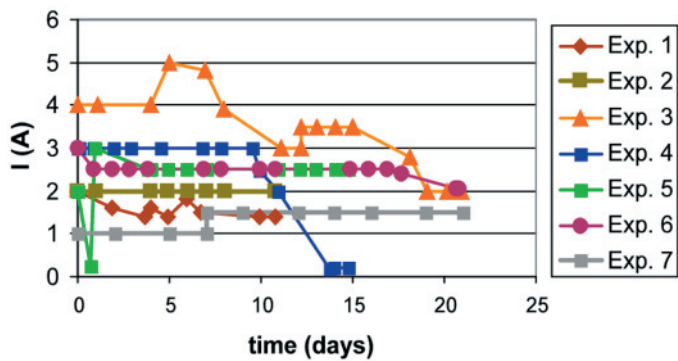


an additive used during remediation or for soaking prior to the electrodialytic remediation. All three wood size fractions were used in experiment 5 in order to evaluate the influence of wood size on the remediation. Experiment 6 was an upscale of experiment 3. The distance between the electrodes was increased from 60 cm to 150 cm and the number of collecting units was increased from 1 to 4 but all other parameters were kept unchanged. Thereby the influence of electrode distance could be evaluated. Experiment 7 was an upscale of experiment 6 but differed also in the wood fractions used. When the two experiments are compared this has to be taken into consideration. Experiment 7 is the largest electrodialytic remediation experiment on wood chips to date.

**Table 2** Experimental Conditions. In Exp. 4 oxalic acid was used as electrolyte solutions. In all other experiments 0.01 M  $\text{NaNO}_3$  was used. Wood fractions: Fine (F) <2 cm, Medium (M) 2-4 cm, Large (L) >4 cm.

	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7
Electrode distance (cm)	60	60	60	60	90	150	270
Wood (kg)	94	106	97	99	178	248	469
Duration (days)	11	11	21	15	15	21	21
Wood fractions	M	M	M	M	F/M/L	M	F
Collecting units	1	0	1	1	2	4	8
Current (A)	1.4-2	2	2-5	0.2-3	2-3	2-3	1-1.5
Voltage (V)	24-25	14-18	30-58	14-60	23-29	40-63	23-39
Middle compartment	Water	Water	Water	5% oxalic acid	Water	Water	Water
Soaking additive /duration (hours)	5% oxalic acid/48	5% oxalic acid/48	0.5 M $\text{H}_3\text{PO}_4$ /18 5% oxalic acid/24	-	0.5 M $\text{H}_3\text{PO}_4$ /18 5% oxalic acid/24	0.5 M $\text{H}_3\text{PO}_4$ /18 5% oxalic acid/24	0.5 M $\text{H}_3\text{PO}_4$ /24 5% oxalic acid/24

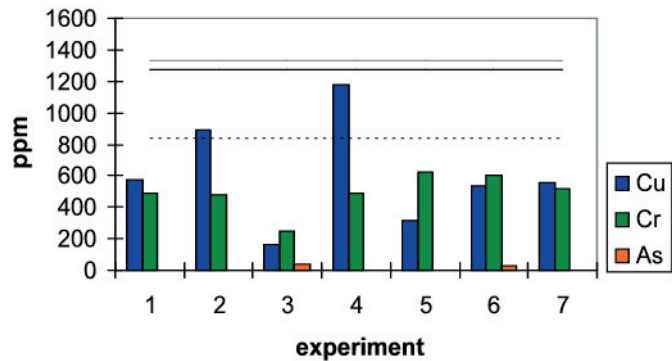
In all the experiments the aim was to keep the current strength as high as possible. In exp. 1 and 2 the max current strength possible was 2 A. For exp. 3-7 the power supply was replaced and the max. current strength was 5 A. In figure 4 the current strength as a function of time is shown for all seven experiments. The current strength was initially kept constant, but during the remediation the current strength was regulated in all experiments but experiment 2, where it was maintained at 2 A. The primary reason for the regulation was that the resistance in the pilot plant increased with time and therefore the current strength had to be reduced. In Experiment 7 the current strength was increased during the remediation. In this experiment it was decided to start the experiment at a moderate current strength of 1 A since it was expected that the large electrode distance would result in a relatively high resistance. This was not the case and during the remediation the current strength was increased to 1.5 A



**Figure 4:** Current strength (Ampere) as a function of time (days) for experiment 1-7.

### 3. Results

The influence of collecting units, soaking, wood size fractions and the electrode distance on the remediation has been investigated. In figure 5 the concentration of Cu, Cr and As in the wood after remediation is shown.



**Figure 5:** The concentration of Cu, Cr and As in the wood after remediation. Concentration of As is only measured in exp. 3 and exp. 6. Horizontal lines indicate initial concentration.

As seen in figure 5 the content of all three metals have been reduced in the wood in all seven experiments. In the following sections the results are discussed in relation to different process parameters.

### 3.1 Collecting Units

In experiment 1 and 2 the setup is similar except for the use of a collecting unit in exp.1. The purpose was to illustrate the influence of the collecting unit on the remediation by comparing the two experiments.

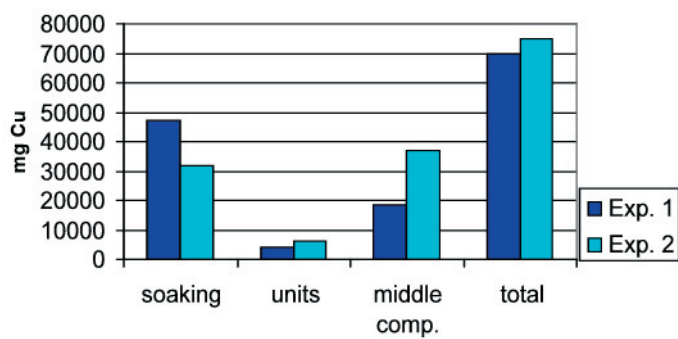
In figure 5 the concentration of Cu and Cr in the wood after remediation is illustrated for all seven experiments. By comparing exp. 1 with exp. 2, it seems that the remediation of Cu was improved by the use of a collecting unit to shorten the way the ions had to travel before being collected. On the other hand, no effect was seen for Cr. To further investigate the remediation, the distribution of removed Cu and Cr after remediation in the two experiments is compared in figure 6.

As can be seen in figure 6a, the total removal of Cr and the amount of Cr present in the units after remediation was similar in the two experiments. However the amount of Cr present in the middle compartment after remediation were higher in exp. 2. This difference is for the most part balanced by the Cr removed during soaking, where the removal seemed larger in exp. 1 where a collecting unit was placed. Cr removed during soaking is not related to the use of collecting units and the seemingly higher removal in exp. 1 compared to exp. 2 may instead be connected with the fact that the soaking liquids from exp. 1 were reused in exp. 2.

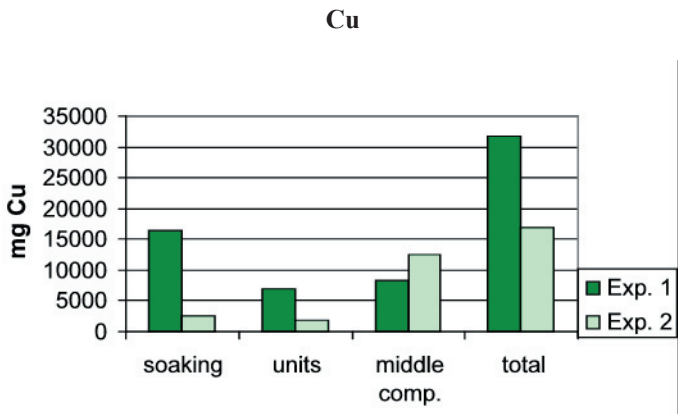
For Cu it was found that a larger amount of Cu was removed in exp. 1 (see figure 6b). The amount of Cu found in the units after remediation was more than three times larger in experiment 1 and the amount of Cu present in the middle compartments was higher in exp. 2, where the ions have to travel a greater distance before being captured in a unit. The reason for the large difference in total Cu removal is not connected with the use of a collecting unit alone. The fact that the soaking liquids from exp. 1 were reused in exp. 2 seemed to play an even larger role for the removal of Cu compared to Cr. The Cu removed during soaking is more than four times larger in exp. 1.

The possibility of reusing soaking solutions have been tested in laboratory scale and the results (not shown) indicated that it may be used up to 4 times without any influence on the remediation efficiency. Thereby no influence by the reuse of the soaking solution was anticipated. However, the apparent reduced removal of Cu and Cr during soaking, when the soaking solution had been used before seems to point in the other direction. Further investigation is needed to verify if the reuse of soaking solutions have an influence on the remediation efficiency. For the present series the soaking solutions has been used and reused three times in total in all experiments except exp. 1 and 3.

Cr



**Figure 6a:** Distribution of removed Cr in experiment 1 (with collecting unit) and experiments 2 (without collecting unit). The term “units” in the figure covers both collecting unit and electrode units.

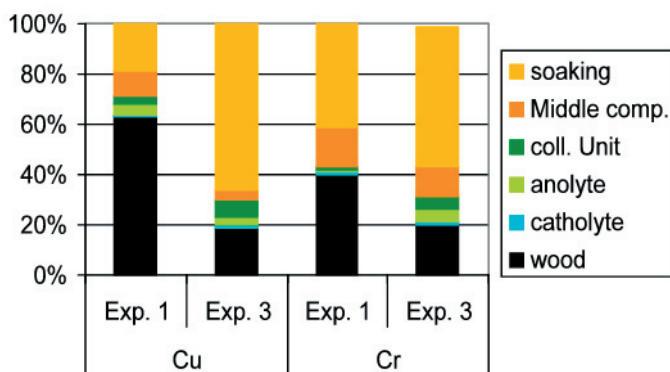


**Figure 6b:** Distribution of removed Cu in experiment 1 (with collecting unit) and experiments 2 (without collecting unit). The term “units” in the figure covers both collecting unit and electrode units.

### 3.2 Soaking

In exp. 4 the wood was not soaked before remediation, but placed directly in the pilot plant. Oxalic acid was used as an additive in the middle compartments and in the units. The experiment had to be stopped after 15 days because of technical problems. The resistance increased dramatically, forcing the current strength to a value below 0.2 A (see figure 4) It was later discovered that the anode was broken. During the experiment the current strength had to be decreased due to extreme gas evolution in the cathode unit that resulted in malfunction of the circulating pump. As seen in figure 5 the remediation of Cu was greatly reduced in this experiment (exp. 4) compared to exp. 1 where the oxalic acid was used in the soaking procedure, and not during the electrodialytic remediation process. In the remaining experiments, soaking was used. Two different additives were tried for soaking in this series. In the first two experiments oxalic acid was used, and in the subsequent experiments dual soaking in phos-

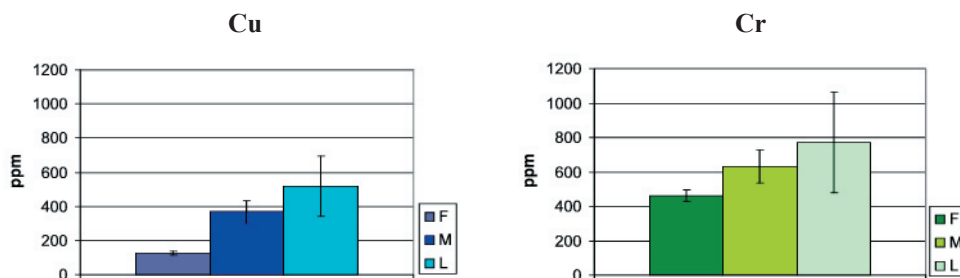
phoric acid and oxalic acid was used. The change in soaking solution was based on a series of laboratory experiments with different acids and combinations of acids, and the use of phosphoric acid, followed by oxalic acids gave the best results in laboratory scale. After remediation only 8% Cu (102 ppm) and 18% Cr (232 ppm) was left in the wood in the laboratory experiment. By comparing exp. 1 and 3 it seems that the change in additive had a profound impact on the remediation (see figure 5). In figure 7 the distribution of Cu and Cr after remediation are shown for exp. 1 and exp. 3. The remediation is increased for both metals by the dual soaking and larger proportions have been removed during soaking in exp. 3 compared to exp. 1



**Figure 7:** Distribution of Cu and Cr after remediation in exp. 1 (oxalic acid soaking) and exp. 3 (dual soaking of phosphoric and oxalic acid).

### 3.3 Wood Size Fraction

In exp. 5 all three wood size fractions was remediated at the same time. The different sizes were evenly distributed all over the pilot plant and after remediation, 24 wood samples from each of the three fractions were analysed for Cu and Cr. The results are shown in figure 8. The final concentration of both metals was significantly lower in the fine fraction than in the medium and large fraction, indicating that it may be easier to remediate wood chips with a size  $< 2$  cm. The concentration of Cu was reduced to  $127 \pm 12$  ppm (mean value  $\pm$  95% confidence limits) in the fine fraction,  $368 \pm 67$  ppm in the medium fraction and  $515 \pm 176$  ppm in the large fraction. Overlap of the 95% CL in the medium and large fraction indicates that the difference between these two fractions was not statistically significant. However the relatively high 95% limits in the same fractions indicate a high variation. For Cr the variation was high in the large fraction where the concentration after remediation was reduced to  $771 \pm 294$  ppm. In the medium fraction the concentration of Cr was  $629 \pm 95$  ppm and  $462 \pm 35$  ppm in the fine fraction. As for Cu, the concentration of Cr was significantly lower in the fine fraction, compared to the medium fraction, indicating an easier remediation of the fine fraction. The high variation in the large fraction did not make the difference between the Cr content of this fraction and each of the other two fractions statistically significant.



**Figure 8:** Concentration of Cu and Cr in wood chips in exp. 5 after remediation ( $\pm 95$  CL), Wood fractions: Fine (F) <2 cm, Medium (M) 2-4 cm, Large (L) >4 cm.

### 3.4 Electrode Distance

For evaluation of the influence of electrode distance on the remediation exp. 3 and 6 are compared. The two experiments had the same duration, and the same wood size fraction and soaking solution were used. In both experiments the max. distance the ions had to travel before being captured was 30 cm, resulting in one collecting unit in exp. 3 and four in exp. 6. The electrode distance was 60 cm in exp. 3 and 150 cm in exp. 6. In figure 5 it is seen that increasing the electrode distance by factor 2.5 results in a decrease in the remediation of approximately the same magnitude for both copper and chromium. The same is not true for the remediation of As. In both experiments more than 95% of the As was removed.

In the laboratory scale the optimum current density for the removal of Cu and Cr from the middle compartment into the electrode compartments was found to be between 0.4 and 0.8 mA/m<sup>2</sup>. If this is to be directly scaled up to the pilot plant membrane size, the optimum current would be 4-8 A. In none of the experiment was the current ever higher than 5 A since this was the max. current possible with the power supply used. Only in exp. 3 was the current ever higher than 3 A, and here it had to be reduced to 2 A in the end of the experiment due to high resistance. In exp. 6 the current was approximately 2.5 A all during the experiment.

The limiting factor when increasing the electrode distance may very well be the current strength and voltage drop. It is likely that the increase in amount of wood and electrode distance may require an increase in electric charge and voltage drop. This was not possible in these experiments due to the all ready mentioned limitations of the power supply.

In exp. 6 only the medium fraction was used and in exp. 7 only the fine fraction was used. In figure 4 it is seen that the remediation in the two experiments seems unaffected by the fact that the electrode distance is 150 cm in one experiment (exp. 6) and almost twice as long (270) cm in the other experiment (exp. 7). The reason for this may have more to do with the difference in wood fraction as discussed in chapter 3.3 than on the difference in electrode distance.

## 4. Discussion

A series of seven electrodialytic remediation experiments has been presented here and different process parameters have been investigated. Due to the limited amount of experiments it is important to emphasize that the results and interpretations may be viewed as tendencies rather than definite conclusions on the matter of remediation in pilot scale.

The use of collecting units to shorten the way the ions have to travel before being captured proved useful, especially in exp. 6 and 7 where the electrode distance was 150 cm and 270 cm respectively. In all but one experiment the wood was soaked in the additive before the electrodialytic remediation process. When soaking was not used, the remediation efficiency decreased and in addition to that, major technical problems were encountered. The purpose of soaking is to remove the most available Cu, Cr and As first and then use the electric current to remove the less available fractions. Soaking solutions contain acid and/or complexing agents in the form of ions that will move in the electric field. If the oxalic acid or phosphoric acid was used directly in the pilot plant a large proportion of the current would be wasted on removing these ions from the middle compartment instead of Cu, Cr and As. By introducing soaking, the wood and CCA comes into contact with the additives prior to that, and the concentration of the acid (ions) in the electrodialytic remediation is reduced. In this series the soaking in phosphoric acid followed by soaking in oxalic acid proved to be most effective.

The reuse of the soaking solutions was initially presumed to have no influence on the remediation, but when the exp. 1 and 2 was compared it seems that the removal of especially Cu during soaking was reduced. When the soaking solution was reused, it is possible that it had become saturated and that some of the Cu precipitated as CuOx during the soaking in exp. 2. Thereby the amount of Cu removed during soaking in exp. 2 may be underestimated in figure 6b. Even if this is the case, the measured concentration in the wood after remediation is still higher in exp. 2 than exp. 1 indicating that the remediation in total was more successful in exp. 1. It may also be interpreted as an indication of precipitation of CuOx in or on the wood chips, and maybe that the precipitate dissolves to a certain extent during the remediation where the wood chips are covered with tap water.

Three different wood size fractions have been remediated and the results indicate that the remediation efficiency increased with decreasing wood size. The remediation of wood chips < 2 cm was significantly better than the remediation of the larger wood sizes. Further investigations are needed to locate the reason but lack of total soaking of the inner part of the larger fractions may be part of it. If the wood is not soaked all the way through, then it is not expected that the current will pass here, since this is believed to be the part of the chip with highest electric resistance. If the soaking solution does not reach the inner part and the current does not pass through, then the CCA will not be removed. To further investigate this possibility, laboratory experiments are planned using vacuum soaking of the wood to insure total soaking prior to the reme-



diation.

In the upscaling process the electrode distance was one of the main factors to be evaluated. The results obtained here indicated that the remediation efficiency decreased with increasing electrode distance. The main problem in estimating the influence of the electrode distance is that the current and voltage drop was similar in all experiments since the current was kept as high as possible in the experiments. The influence by the voltage drop on the remediation efficiency could not be evaluated, since the voltage drop is similar in the two extremities. Instead a power supply with a higher voltage range is needed for these experiments, to ensure that the V/m may be the same in the experiments to be compared. The use of collecting units is expected to insure that the remediation time is unaffected by the electrode distance, since the distance the ions have to travel before being collected may be the same. This theory has to be verified with the above mentioned power supply.

The highest removal of both Cu, Cr and As was obtained in exp. 3, where 87% Cu, 81% Cr and more than 95% As was removed during remediation, resulting in concentrations of 163 ppm Cu, 252 ppm Cr and less than 43 ppm As in the wood after remediation. In this experiment the electrode distance was 60 cm and just under 100 kg wood chips of medium size fraction (2-4 cm) was used. When the electrode distance was increased, the removal of Cu and Cr was decreased. In exp. 6 where the electrode distance was 150 cm and 250 kg wood was remediated, 58% Cu and 54% Cr was removed. On the other hand the remediation of As didn't decrease with increasing electrode distance. In the same experiment 96% As was removed. This is a very encouraging result since As is the CCA component of most concern and the main reason why incineration of CCA-treated wood is not allowed in Denmark. If the remediated wood is to be used as a bio fuel, it is assumed that the concentration of Cu, Cr and As must be reduced to practical zero value first. Instead it is possible that wood, where As has been removed and the concentration of Cu and Cr are reduced can be used in a conventional waste incineration plant. Thereby the energy resource of the wood may still be utilised.

## 5. Conclusion

CCA-treated wood chips was subjected to Electrodialytic remediation in a series of 7 pilot scale experiments. Several process parameters were investigated and based on the experiments it was concluded that the use of collecting units was beneficial to the remediation. Soaking proved desirable for the process and dual soaking by phosphoric and oxalic acid was more efficient than oxalic acid alone. The possibility of reusing the soaking solutions has to be investigated further. The remediation of wood chips < 2 cm was significantly better than the remediation of the larger wood sizes. The removal of Cu and Cr decreased with increasing electrode distance, whereas the remediation of As seemed unaffected by the increase in electrode distance from 60 cm to 150 cm.

The highest removal of both Cu, Cr and As was obtained in exp. 3, where 87% Cu,

81% Cr and more than 95% As was removed. In this experiment the electrode distance was 60 cm and the wood was soaked in phosphoric acid and oxalic acid prior to the electrochemical remediation.

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# The influence of metal pieces on the electrodialytic removal of Cu and Cr from CCA-treated waste wood

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## Abstract

The scale up of Electrodialytic Remediation (EDR) of CCA-treated wood makes it desirable to use industrial available methods for the shredding of waste wood prior to EDR. Even though these methods often include a magnetic separation to remove metal objects from the wood chips, several pieces of metal, including iron nails and copper wires were observed in the wood chips after the separation. Since an electric field is applied during EDR, it was considered necessary to investigate if the removal of Cu and Cr was affected by the presence of metallic iron or metallic copper. The results indicate that the removal of Cu and Cr was not altered by the presence of 3.6% metallic iron or 0.9% metallic copper in the wood chips during remediation. The amount of metallic iron and copper in these experiments exceeded the amount found in practise by a factor 10 and 100 respectively. It is still recommended that the majority of the metal objects are removed by magnetic separation, since large fractions are expected to influence the remediation and disturb the electric field.

## Keywords

Electrodialytic remediation, CCA-treated wood, metallic iron, metallic copper

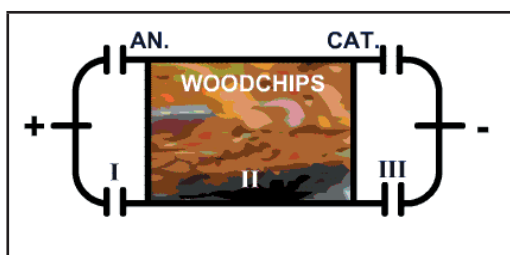
## Introduction

When CCA-treated wood is removed from service, the contents of copper, chromium and arsenic is still high in many cases, due to a strong fixation of CCA in wood. In order to maintain CCA-treated wood as an attractive building material, it will be beneficial to develop methods for environmental safe handling of the wood waste and preferable reuse of the resources the wood contains (energy, copper, chromium and arsenic).

In Denmark the incineration of CCA-treated waste wood is banned and deposition in landfills is the only alternative, until new methods have been introduced that ensures reuse of the wood resources (energy and metals).<sup>1</sup>

## Electrodialytic remediation

Electrodialytic remediation is a method developed at the Technical University of Denmark for cleaning soils polluted with heavy metals. The method uses a direct electric current as cleaning agent and combines it with the use of ion exchange membranes to separate electrolytes and soil.<sup>2,3</sup> Figure 1 shows the electrodialytic cell in principle.



**Figure 1:** Schematic presentation of an electrodialytic cell. Compartment I and III is the anode and cathode compartment, compartment II contains the wood chips.

AN: Anion exchange membrane. CAT: Cation exchange membrane.

The laboratory cell consists of three compartments: an anode compartment (I), a cathode compartment (III) and a middle compartment (II) with the wood chips, placed between these. The catholyte is separated from the middle compartment by a cation exchange membrane (a membrane that only allows positive ions – cations to pass) and the anolyte is separated from the middle compartment by an anion exchange membrane (which allows only negative ions – anions to pass).

When an electric potential is applied to the system the current in the cell will be carried by ions in the solutions of the compartments, and the ions will move in accordance to their charge. Cationic species will move towards the cathode and anionic species will move towards the anode. The ion exchange membranes ensure that no current carrying ions can pass from the electrode compartments into the middle compartment, while ions can be transported from the middle compartment into the electrode compartments. In this system current is thus prevented in carrying highly mobile ions from one electrode compartment through the middle compartment into the other electrode compartment. Furthermore competition between these highly mobile ions from the electrode compartments and the ions in the middle compartment is avoided.

Good results have been obtained using this method for remediation of heavy metal polluted soil, and subsequently the method has been tested for treatment of other materials e.g. fly ash, sludge and most recently CCA-treated waste wood. The first remediation of CCA-treated waste wood was performed with sawdust. The results were very promising with 93% Cu, 95% Cr and more than 99% As, removed at the



end of the 30 days experiment.<sup>4</sup> Subsequently the method has been applied to wood chips. By using woodchips instead of sawdust, less processing of the treated wood is required. Thereby the workers doing this will not be exposed to airborne particles to the same degree, and a safer work environment will be created. The results with wood chips were very promising too. At the end of a 7 days laboratory scale experiment, 94% Cu and approximately 85% of both Cr and As was removed.<sup>5</sup> The method has now been tried in pilot scale and in an experiment with approximately 100 kg wood chips, 87% Cu, 81% Cr and more than 95% As was removed<sup>6</sup>

The wood that was used in the pilot plant was supplied by RGS90, the largest recycling company in Denmark. From a large pile of demolition wood waste 10 m<sup>3</sup> of impregnated wood was collected and Chromazurol S, a colour reagent that turns blue in contact with Cu, was used to identify the impregnated wood. After sorting and shredding, the wood chips were subjected to magnetic separation to remove metallic contamination. However, several pieces of metal (nails, copper wire etc.) were observed in the wood chips after the separation. Since the procedure used here (sorting, shredding and magnetic separation) represents the conditions that could be expected in industrial scale shredding of wood, it is most likely that the presence of metal pieces in the wood chips during electrodialytic remediation can not be avoided in the future, both due to incomplete separation of (magnetic) metal and wood, and the presence of metals (e.g. Cu) that is not removed by the magnetic separation. The experiments presented here are designed to evaluate how the presence of metal pieces in wood chips may influence the electrodialytic remediation process.

## The influence of metal pieces on the electric field of EDR

If pieces of metallic iron or metallic copper are placed in the middle compartment during an EDR experiment, the electric field is most likely influenced. In EDR the current is carried by ions in a solution, while electrons are responsible for passing the current in metal.

Metallic iron or copper will act as a conductor in the electric field generated in the EDR cell. When a conductor is placed in the middle compartment of the EDR cell, part of the current will pass through it, due to lower resistance in the metal compared to the solution and wood. Inside the metal piece a delocalization of charge will take place in response to the external electric field and this will result in the formation of an anode and cathode area of the metal piece.

The end of the metal piece that points towards the cathode of the EDR cell will function as a local anode with oxidation of the metallic iron or copper ( $\text{Fe}^0$  to  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  or  $\text{Cu}^0$  to  $\text{Cu}^+$  or  $\text{Cu}^{2+}$ ). The end that points towards the anode will function as a cathode where metal ions from the solution may be reduced. The presence of a anode and cathode part of a metallic object when placed in the EDR electric field has been observed when a screw was present in the middle compartment during EDR of soil.<sup>7</sup>

## Experimental section

A series of three experiments were conducted and represent the situation of wood without metal pieces; with a piece of metallic copper; and with metallic iron respectively.

### Wood

For this series of experiments wood chips made from the outermost 3 cm of an out of service electricity pole were used. The pole was a *Picea abies* L. treated with 12 kg K33 (CCA-B) pr m<sup>3</sup> sapwood in 1962 by Collstrop A/S. The pole was removed from service in 1999. All nails and other metal pieces were removed by hand before the wood was chipped.

### Analytical methods

The concentration of Cu and Cr was measured in the wood chips before and after remediation by Atomic Absorption Spectroscopy (AAS) after microwave assisted acid digestion of wood chips samples. Each sample weighted 0.25 g and was digested in 10.0 ml of concentrated nitric acid. Prior to AAS measurement the sample was diluted to a final volume of 25.0 ml with distilled water.

### Electrodialytic remediation

Prior to the electrodialytic remediation, the wood was soaked in 5% oxalic acid for 18 hours. Then the wood chips was placed in the middle compartment (II) of the electrodialytic cell (see figure 1). The middle compartment was a Plexiglas cylinder (10 cm long, 8 cm ID) and the wood chips were covered with 0.25% oxalic acid. Platinized electrodes obtained from Bergsøe Anti Corrosion were placed in the electrode compartments (I and III). In each electrode compartment 0.01 M NaNO<sub>3</sub> was circulated during the remediation. The membranes were from Membranes International and were placed according to figure 1. During the remediation pH was measured daily in the electrode compartments and adjusted to just below pH 2 if necessary.

In table 1 the experimental condition for the experiments are outlined.

**Table 1:** Experimental conditions for electrodialytic remediation (EDR) experiments

m wood	70 g
Duration (EDR)	3 days
Soaking solution	400 ml 5% oxalic acid
Duration (soaking)	18 hours
Additive (middle compartment)	300 ml 0.25% oxalic acid
Anolyte	1 L 0.01 M NaNO <sub>3</sub>
Catholyte	1 L 0.01 M NaNO <sub>3</sub>
Current (constant)	30 mA

The three experiments differed in the presence of a metal piece in the wood chips during remediation:

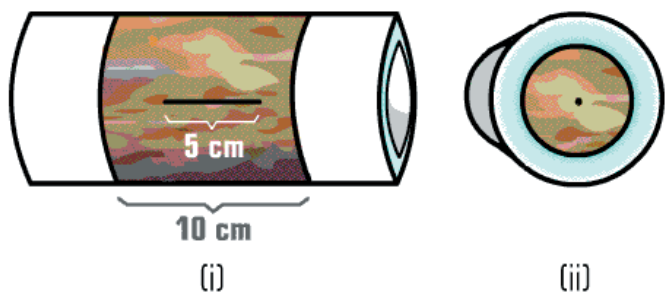
- **Experiment A** contained no metal pieces and served as a reference experiment.
- In **Experiment B** a 5 cm long iron nail was placed according to figure 2.
- In **Experiment C** a 5 cm long copper wire was placed according to figure 2.

An iron nail was chosen for experiment B as opposed to e.g. a steel nail, in order to minimise the contamination of the system with additional Cr from the nail. By avoiding this, the comparison of the Cr removal in the three experiments will be easier, since the only Cr present in all three experiments will be from the CCA in the wood. In practise steel nails are used instead of iron nails, due to corrosion of iron nails in connection with CCA treated wood for outdoor use. The copper wire and iron nail was weighed before and after remediation.

To estimate the actual amount of metallic iron and copper that is present in the wood chips after magnetic separation, two batches of wood chips from the process described earlier (see Introduction) were sorted by hand. Each batch weighed approximately 6 kg and metallic iron was found in both batches, as nails, screws and metal plates. In the two batches the amount of this kind of metal was 4.96 g and 15.45 g or 0.08% and 0.3% respectively of the wood chip batches.

Metallic copper was only found in one of the bathes and in very small quantities (0.86 g, 0.01%) but in both batches plastic coatings from copper wires were found and therefore it is suggested that higher amounts of metallic copper may be present in other wood chips batches.

The amount of metallic iron and cooper to be used in experiment B and C was deliberately exceeded compared to the actual findings. Thereby the fact that only two batches were investigated is taken into account and at the same time the experiments may be evaluated as a worst case scenario. The amount of metallic iron in experiment B correspond to 3.6% and the metallic copper in experiment C accounts for 0.9% of the total weight in the middle compartment. The mass of the metal pieces are given in table 2.



**Figure 2:** Schematic presentation of position of the iron nail and the copper wire in the middle compartment of experiment B and C respectively. [i] Side view, [ii] end view.

## Results and discussion

### Metal pieces

After remediation the metal pieces was removed from the middle compartment. Yellow precipitations were found on the iron nail, whereas the copper wire seemed unaffected. In table 2 the mass of the metal pieces are shown. For the iron nail, the mass after removal of the yellow precipitate are given in brackets.

**Table 2:** Mass of metal pieces before and after remediation.

Experiment	Mass before remediation	Mass after remediation
B iron nail	2.62 g	2.67 g (2.57 g)*
C copper wire	0.66 g	0.66 g

\*weight of iron nail after removal of yellow precipitates.

### Iron nail

The appearance of the iron nail was clearly altered after the electrodialytic remediation. A yellow precipitate with a total weight of 0.1 g (corresponding to almost 4% of the total weight of the nail) could be removed after scraping with a spatula. The chemical composition of the precipitate is unknown but iron(II)oxalate ( $\text{FeC}_2\text{O}_4$ ) is a possibility. Iron(II)oxalate is a yellow precipitate and has a low solubility ( $K_{\text{sp}} = 2.1 \times 10^{-7} \text{ M}^2$ ). Another possibility is the formation of iron(III)arsenate ( $\text{FeAsO}_4$ ) which is also a yellow precipitate with low solubility ( $K_{\text{sp}} = 5.7 \times 10^{-21} \text{ M}^2$ ).

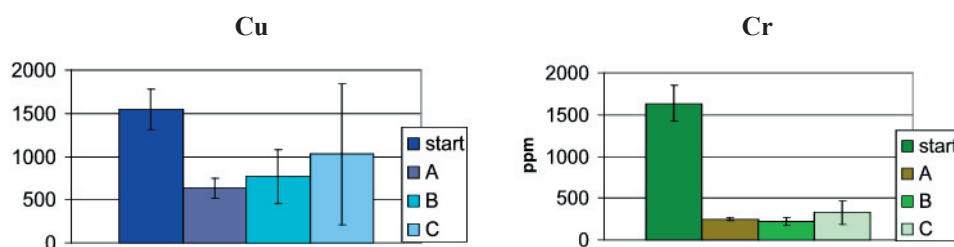
The spread of the precipitate was found to be confined to the end of the nail that functioned as an anode and covered no more than 1/3 of the nail. This is in agreement with the theory of oxidation of  $\text{Fe}^0$  at the anode end of the nail. No visible alteration of the cathode end of the nail was observed. Theoretically Cu (and Cr and Fe) ions from the solution could be reduced at this end of the nail.

## Copper wire

No reduction in the mass of the copper wire could be detected in experiment C as a result of the electrodialytic remediation. No apparent change in the Cu surface was detected after remediation, despite the fact that metallic copper wire may form a local anode and cathode like it was the case for the iron nail. The fact that no change in mass of the copper wire could be detected does not mean that no reactions (oxidation and reduction) took place. It may alone imply that the two reactions were (close to) mass equivalent e.g. oxidation of  $\text{Cu}^0$  to  $\text{Cu}^{2+}$  at the anode end and reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  at the cathode end. Other reactions may also have occurred and the findings are most likely due to a combination of different reactions rather than only one.

## Concentration of Cu and Cr in wood after remediation

The concentration of Cu and Cr before and after remediation is shown in figure 3

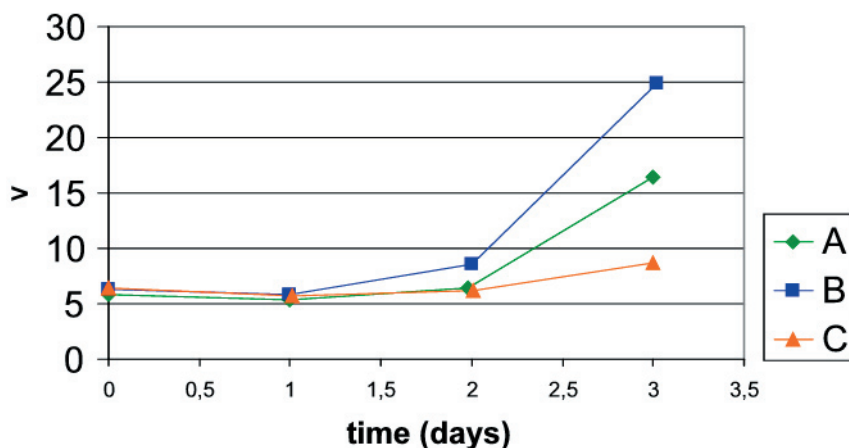


**Figure 3:** Concentration of Cu and Cr in wood before and after remediation. Mean value of 6-15 measurements  $\pm$  95 % CL. Experiment A: Reference, B: with iron nail, C: with copper wire.

In all three experiments the concentration of Cu and Cr has been reduced after remediation. The removal of Cu seems to be less efficient with the presence of the iron nail and especially the copper wire, but the difference in concentration of Cu is not statistically significant (95% CL) in the three experiments. The large confidence interval in experiment C, with copper wire present during the remediation, may be taken as a confirmation that the copper wire was in some way affected by the electric field. It may imply that Cu ions are removed by oxidation at the anode and maybe precipitated on/inside the wood as copper oxalate. If this is taking place locally, then the high variation, that lead to the large confidence limits may be due to this. The removal of Cr seems unaffected by the presence of iron or copper pieces. Like for Cu, there is an overlap of the confidence limits for the three experiments, and based on the mean value, the difference between the experiments are much less pronounced for Cr compared to Cu.

## Current and voltage drop

In all experiments the charge consumption has been the same, due to a constant current and similar duration of the experiments. In figure 4 the voltage drop for the three experiments is shown as a function of time.



**Figure 4:** Voltage drop as a function of time. A: reference. B: iron nail C: copper wire

In all experiments the voltage drop were fairly constant during the first two days of the experiment and increased during the final day. The increase is probably due to lack of easily removable ions in the middle compartment after two days. The voltage drop is highest when an iron nail is present and the fact that a precipitate is formed here, may partly explain the higher resistance in the experiment, since ions are removed to form a precipitate. However the variation in the three experiments is well within the variation normally observed in the laboratory and care should be taken in interpretation of these differences.

## Conclusion

Based on the three experiments presented here, no difference in the removal of Cu and Cr can be attributed to the presence of relatively small amounts of metallic iron or copper. However, the variation in the concentration of Cu that was measured in the experiment where a copper wire was present during EDR, resulted in 95% CL that made it statistically impossible to distinguish between the concentration before and after remediation.

In the case of the iron nail, a yellow deposit was precipitated on the nail during remediation. If the precipitate contains As, the removal of As will be influenced by the presence of metallic iron.

It is still recommended that magnetic sorting is used when preparing wood chips for electrodialytic remediation in order to reduce the amount of metal pieces to a minimum. An effect is expected if high concentrations of metal objects are present in the electrodialytic cell, at least the electric field is expected to be disrupted by the presence, due to the lower electric resistance of the metal pieces compared to the solution

in the middle compartment.

## Acknowledgement

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# Reusing process liquids from electrodialytic remediation for impregnation of new wood

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## Abstract

Electrodialytic remediation can be used for the removal of copper (Cu), chromium (Cr) and arsenic (As) from CCA-treated waste wood. The removed metals are collected in liquids after remediation. These process liquids are often high in volume but low in concentration, which makes recovering of the metals costly. In the present paper the possibility of reusing the liquids directly for impregnation of new wood is investigated. Different types of process liquids were tested for the use as make-up water in stead of tap water normally used when a CCA stock solution is diluted to a 2% CCA working solution. In all solutions an acceptable pH was obtained compared to the reference solution where tap water was used as make-up water. However precipitation of Cu and Cr was observed in process liquids that contained oxalic acid. The leaching of Cu and Cr was measured according to EN 84:1997 and even though the leaching was low when electrolytes and liquids from the middle compartment was used, final concentrations of Cu was significantly lower in all the experiments compared to the reference experiment. It is concluded that the process liquids tested here needs optimisation before they can be used. Optimisation may include anodic oxidation of oxalic acid and oxidation of Cr(III) to Cr(VI) by conventional oxidising agents like hydrogen peroxide.

## Introduction

In the resent years the possibility of removing copper (Cu), chromium (Cr), and arsenic (As) from CCA-treated waste wood by electrodialytic remediation (EDR) has been investigated and with promising results (*Ribeiro et al 2000, Kristensen et al 2001*). In a pilot scale experiment where approximately 100 kg wood chips were used, a removal of 87% Cu, 81% Cr and > 95% As was obtained (*Christensen et al. 2004*). After remediation the removed Cu, Cr and As are located in the various process liquids (soaking solutions, electrolytes and the water in the middle compartment).

One of the main goals when using EDR is to avoid the creation of new waste products and the Cu, Cr and As may be recovered from the above mentioned process solutions either by electro-deposition or precipitation (*Hansen 2000*) but the fact that in many cases the volumes are high and the concentration of Cu, Cr and As is low, makes it interesting to examine the possibility of reusing the process liquids directly instead of recovering the metals first.

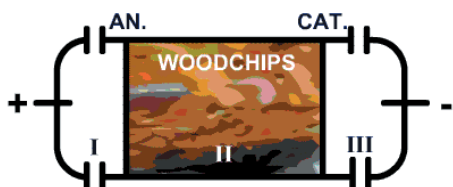
All process liquids were aqueous solutions and apart from varying concentrations of Cu, Cr and As other components (additive etc.) will also be present depending on the nature of the process liquid.

## Soaking solutions

In EDR an additive (acid and/or chelating agent) is used to facilitate the removal of CCA from the wood. Prior to EDR the dry wood was soaked in 0.5 M phosphoric acid, followed by another soaking in 5% oxalic acid. After soaking the solutions will still contain high concentrations of the additive as well as a fraction of extracted Cu, Cr and As. It may also contain small pieces of wood and other extracted materials from the wood (organic and inorganic).

## Electrolytes and middle compartment liquids

The electrodialytic setup is presented in figure 1. After soaking the additive saturated wood, were placed in the middle compartment of the EDR cell where it was covered with tap water. During EDR the CCA will move from the wood into the water in the middle compartment and from the middle compartment into the electrolytes (0.01 M  $\text{NaNO}_3$ ) in the electrode compartments. After the EDR process part of the Cu, Cr and As was located in the electrolytes but some was still found in the liquid in the middle compartment. Given that the wood was saturated with additive, this would also be present in the solutions although in much lower concentration than in the soaking solutions.



**Figure 1:** Schematic presentation of an electrodialytic cell. In compartment I and III the electrodes are placed and electrolyte solutions (0.01 M  $\text{NaNO}_3$ ) is circulated. Compartment II contains the wood chips.

AN: Anion exchange membrane. CAT: Cation exchange membrane.

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## Aim of present paper

The aim of the present paper is to evaluate the possibility of reusing the process liquids from EDR directly for impregnation of new wood.

When wood is impregnated with CCA, a 2% working solution of CCA is produced by diluting a CCA stock solution with make-up water. Normally ordinary tap water is used, but here the possibility of using different process liquids instead was investigated.

The 2% working solutions were used to impregnate wood test specimens (EN113) and subsequently a leaching test is performed to evaluate the effect of using process liquids as make-up water.

## Experimental section

### Preparation of CCA working solutions

A series of 2% CCA working solutions was prepared from a stock solution by mixing 17.6 ml Celcure CCA-C 50% and 982.4 ml make-up water. A total of five solutions were made and the identity of the make-up water and the concentration of Cu and Cr are presented in table 1. The concentration of As has to be measured at an external laboratory and this will be done at a later stage in the experiments where encouraging results are obtained for Cu and Cr.

The solution for experiment A was made with tap water and served as a reference experiment. In experiment B and C a soaking solution that contained phosphoric acid was used in different concentrations. Before soaking of the wood the concentration of phosphoric acid was 0.5 M. In experiment D a solution from the middle compartment is used. In experiment E an electrolyte solution is tested. The solutions came from different pilot scale EDR experiments, but with similar experimental conditions regarding soaking and additives. (*Christensen et al. 2004*)

The concentrations of Cu and Cr in the solutions are shown in table 1.

It was not possible to use soaking solutions that contained oxalic acid as make-up water. Even if the soaking solution was diluted 1:10 before mixing green precipitations were formed almost immediately and the use of this as make-up water was rejected.

**Table 1:** Identity of make-up water in the test solutions. Solution A is the reference solution, where only tap water was used. [Cu] and [Cr] are the concentrations in the make-up water.

Experiment	Make-up water	[Cu] (ppm)	[Cr] (ppm)
A	Tap water	0	0
B	Soaking solution containing $\text{H}_3\text{PO}_4$ .	168	64
C	Soaking solution containing $\text{H}_3\text{PO}_4$ , mixed with tap water 1:1	84	32
D	Middle compartment solution, mixed with tap water 1:1	21	81
E	Electrolyte solution mixed with tap water 1:10	2	11

## Impregnation of wood

Five EN113 test specimens (50 mm x 25 mm x 15 mm) were impregnated in each experiment. The test specimens were impregnated in a vacuum desiccator (4 kPa for 20 min) and remained in the CCA solution of two hours. Then the wood was placed in a conditioning chamber ( $20 \pm 2$  °C and  $65 \pm 5$  % relative humidity) for 14 days to allow for fixation of CCA. For the first week the wood was kept in black plastic bags to prevent drying of the wood during this time.

## Leaching tests

The leaching tests were performed approximately one month after impregnation of the wood.

An European leaching standard (*EN 84:1997*) was used. First the wood was vacuum treated with water, following the same impregnation procedure as described above and after leaving the wood specimens in the water for two hours, the water was replaced. During the following 14 days, the water was replaced a total of 10 times. The volume ratio of water to wood was 5:1, resulting in 500 ml water in each experiment with five test specimens.

## AAS

The content of Cu and Cr in the wood after leaching was measured by Atomic Absorption Spectroscopy (AAS) after a microwave assisted acid digestion of four samples from each experiment (0.4 g wood in 10.0 ml conc.  $\text{HNO}_3$ , diluted to 25.0 ml with water prior to AAS). Aqueous samples were preserved with  $\text{HNO}_3$  (4:1) prior to AAS. The concentration of As were not measured at this time.



## Results and discussion

### 2% CCA solutions

Prior to the impregnation of the EN113 test specimens, the 2% working solutions were characterised with regards to pH, density and concentration of both Cu and Cr. The results are given in table 3. In solution D and E a light green precipitate had formed during the period of one week from the mixing of the solutions to the impregnation. AAS Analyses after pressure assisted acid digestion of a sample showed that both Cu and Cr were present in the precipitate, but no quantitative analysis was made.

**Table 3:** Concentration of Cu and Cr, pH and density of the five solutions prior to impregnation

Solution	Cu (ppm)	Cr (ppm)	pH	Density (g/ml)
A (reference)	1649	2565	2.08	1.01
B	1834	2453	1.78	1.04
C	1750	2289	1.94	1.02
D	1331	2566	2.22	1.01
E	1272	2606	2.09	1.01

When comparing the actual measured concentrations in the working solutions (table 2) with the concentrations in the make-up water (table 1) some of the variations may be explained.

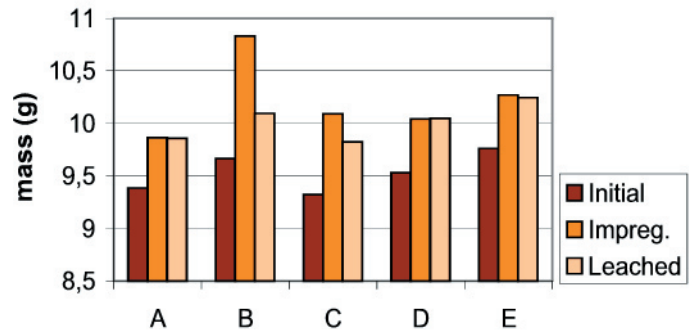
The concentration of Cu was slightly increased in solution B and C, and reduced in solution D and E, compared to the reference solution. The increase of Cu in solution B and C reflect the fact that the make-up water contained some Cu and that no precipitation was observed. In solution D and E where the Cu concentration was decreased, a precipitate containing copper was observed. The variation of Cr in the test solutions compared to the reference did not follow the same pattern. In solution D and E, where chromium-containing precipitate was formed, the concentration was not reduced compared to the reference solution. In solution B and C, the concentration of Cr was slightly decreased compared to the reference solution, even though no visible precipitate or other reasons for the apparent decrease in Cr were observed. The explanation is not obvious and further investigations are needed in order to locate the reasons.

The pH in the reference solution was 2.08 and in solution B to E the pH was between 1.78 and 2.22. This is well within the recommended pH interval of 1.7-2.5 (*Hartford 1986*).

# Impregnated wood

The specimens were weighed before and after impregnation and after leaching experiments.

In figure 2 the results are presented by mean values of the five samples in each series.

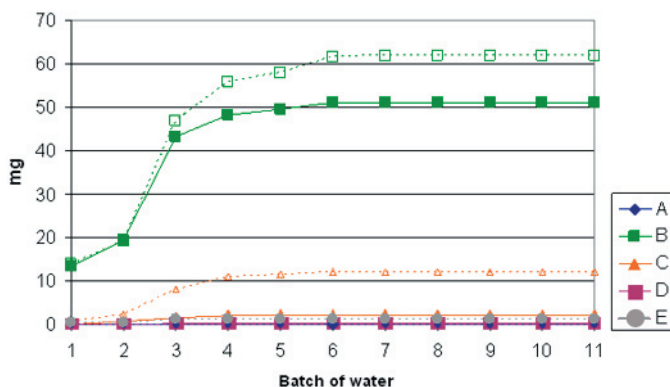


**Figure 2:** Mass of wood specimens before and after impregnation and after leaching. Presented as a mean value of the five samples in each experiment

The uptake is higher when phosphoric containing process liquids were used as make-up water (B and C) especially in (B) where there was no dilution of the process liquids. After leaching the mass decreases to a level similar to the control series. The increased uptake and leaching may at least in part be due to the phosphoric acid present in the make-up water. Since the process liquid has a high concentration of phosphoric acid, some will most likely be taken up by the wood during impregnation and thereby adding to the total mass of the impregnated sample before leaching. However phosphoric acid is not expected to be fixed in the wood like Cu, Cr and As and the majority will eventually be removed from the wood during the leaching experiment. In the reference experiment (A) and experiment D and E, the weight did not decrease after leaching.

## Leaching of Cu and Cr

The concentrations of Cu and Cr were measured in the water after leaching. The accumulated amount of Cu and Cr in the leaching water as a function of batch of water can be seen in figure 3.



**Figure 3:** Accumulated amount of Cu and Cr leached as a function of batch of water for experiment A-E. Cu: dotted line, Cr: solid line.

The leaching of Cu is higher than Cr in all cases where leaching was observed. The leaching was highest in the first three batches of water and in no cases was there observed any leaching after the water had been changed five times (six batches). The leaching of Cu and Cr was highest when soaking solutions were used as make-up water (B and C). When solutions from the middle compartment (D) was used, the leaching was very low and when diluted electrolytes were used (E), the leaching was not detectable. The fact that the leaching was zero in the reference (A) were reassuring and expected!

Based on the results from the leaching tests, soaking solutions (B and C) was not suitable as make-up water, not even when a diluted version of the soaking solution was used (experiment B).

The high leaching of Cu and Cr seems to indicate low fixation in the wood:

The fixation of CCA is close connected to the reduction of Cr. The driving force of the strong fixation of CCA in wood is the reduction of Cr(VI) to Cr(III).

In CCA formulations Cr is present as Cr(VI) and during the reduction of Cr(VI) to Cr(III), sites in the wood will be oxidised and strong fixation sites for Cu and As may be created.

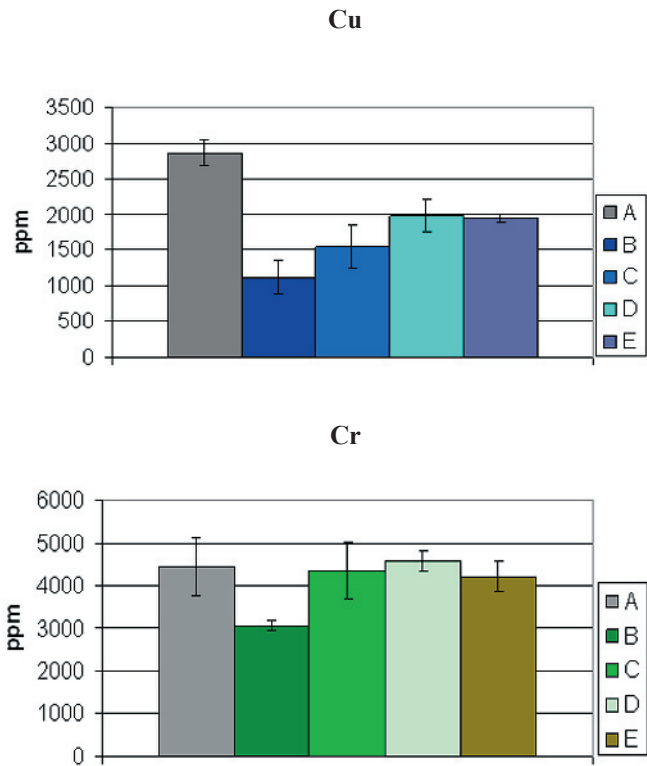
While As is most often found in connection with Cr (e.g. as  $\text{CrAsO}_4$ ) the majority of Cu (80-90%) are found to be fixed to the wood, independent of Cr and As. (Pizzi 1982)

If part of the reduction of Cr(VI) to Cr(III) takes place outside the test wood specimen, e.g. by reduction of organic components or small pieces of wood that is present in the make-up water (soaking solutions) then fewer sites will be created for fixation of Cu, resulting in part of the Cu being able to leach. The Cr that is present in the make-up water will be present as Cr(III) and may also leach.

Another explanation is the fact that the soaking solutions also contained phosphoric acid, and this was used as an additive during EDR to facilitate the extraction of CCA from wood. It seems likely that the phosphoric acid in the make-up water may be responsible for the extraction of Cu and Cr, if not by inhibiting the fixation, then by extraction during leaching.

When liquids from the middle compartment or electrolytes were used as make-up water (experiment D and E) very low leaching was observed. This could be seen as an indication of strong fixation of CCA. However, given the fact that a precipitate that contained both Cu and Cr was formed in the working solutions during the first week after mixing may also indicate that the low leaching was due to low content of Cu and Cr in the impregnated wood.

Therefore the concentration of Cu and Cr was also measured in the wood after leaching to evaluate if the reason for the low leaching is strong fixation or lack of CCA uptake. The concentration of Cu and Cr in the wood after remediation is illustrated in figure 4.



**Figure 4:** Concentration of Cu and Cr in wood after leaching. Presented as the mean value of 4 samples  $\pm$  95% CL.

When figure 4 is compared to figure 3, it is obvious that soaking solution (B) is not suited as make-up water. Leaching of both metals is high and the concentration in the wood is highly reduced compared to the reference experiment (A). In diluted form (C) the soaking solution must be rejected due to the low concentration of Cu.

This is also the case when solutions from the middle compartment (D) and electrolytes (E) are investigated. The concentration of Cu is approximately 2/3 of the concentration in experiment A and it seems unlikely that this would be tolerated in commercial CCA impregnation. In addition to that, part of the CCA precipitated when liquids from the middle compartment (D) and electrolytes (E) were used.

The difference in the composition of the make-up water may be a possible explanation for the formation of precipitates in experiment D and E but not in A and B. The electrolytes and middle compartment liquids may contain oxalic acid, since the wood was soaked in oxalic acid after soaking in phosphoric acid, but prior to being placed in the EDR set-up.

Preliminary testing showed that the oxalic acid slaking solutions could not be used as make-up water since precipitations were formed almost immediately. The reason it is not observed immediately in experiment D and E may be the much lower concentration of oxalic acid in these solutions. Besides from precipitating with Cu, oxalic acid may be responsible for reduction of Cr(VI) to Cr(III) and subsequently Cr(III) may precipitate with Cu and or As.

The precipitation of the CCA working solution in industrial scale impregnation are also known. These sludges are often connected with the reduction of Cr(VI) to Cr(III) by e.g. wood components in the recycled CCA solution and subsequently precipitation involving Cr, Cu and As are formed. (*e.g. Kazi & Cooper 2002*).

It is evident that the process liquids from EDR that has been tested here are unsuitable as make-up water in the present form but may need to be optimised before use. Some suggestions to the optimisation of the liquids are presented here:

The presence of Cr(III) can cause sludging of the CCA solution and therefore the presence of Cr(III) should be avoided. *Kazi & Cooper (2002)* propose that Cr(III) may be oxidised to Cr(VI) by sodium hypochlorite and *Pizzi (1996)* suggest hydrogen peroxide or potassium permanganate. This may also be applicable to the treatment of the process liquids before they are mixed with the CCA stock solution.

Another problem with the process liquids is the presence of an additive, because it was used to extract the CCA during EDR. Especially oxalic acid seems to be a problem, even when the process liquids were diluted first, precipitations were still formed. The presence of oxalic acid may cause reduction of Cr and therefore it seems evident that oxalic acid is removed before the reuse. Oxalic acid may be removed by anodic oxidation, and the rate of removal greatly depends on the electrode material. For instance *Bock et al. (2002)* finds that the use of a tungsten oxide based anode results in a more rapid removal of oxalic acid than antimony doped anodes.

## Conclusion

The results presented here are based on a limited selection of process liquids but the results seem to indicate that some kind of optimization of the EDR process liquids are needed before they can be used as make-up water in the wood preservation process. One of the main problems is that during EDR additives (oxalic acid and phosphoric acid) are used to facilitate the removal of CCA from wood. After remediation these additives will still be present in the process liquids in various concentrations. The presence of oxalic acid seemed to be most problematic. Even in process liquids with low concentrations of oxalic acid, precipitation that involved both Cu and Cr occurred. Reduction of Cr(VI) to Cr(III) by oxalic acid is possible and could result in precipitation similar to the sludging observed industrially when Cr(III) is present in a CCA working solution. Oxalic acid may be removed by anodic oxidation if the right anode material is chosen (*Bock et al. 2002*). Soaking solutions that contained phosphoric acid resulted in high leaching of Cu and Cr. If these solutions are to be used as make up water the phosphoric acid should be removed first. If this is too complicated these liquids may be more suited for recovering of the metals instead of directly reused for wood preservation.

In all process liquids Cr is present as Cr(III) and it may be beneficial to oxidise Cr(III) to Cr(VI) before mixing the CCA stock solution with the process liquids, since Cr(VI) is needed for the fixation process. Several oxidizing agents seem to be suited for this process.

Before the usability of optimised versions of the process liquid can be evaluated, further experiments, including biological tests are needed in order to give a more comprehensive picture.

Also measurements of As has to be included, since this is an important component of CCA and also the CCA-component of the highest environmental concern.

## Acknowledgements

Lars Nyborg from Osmose DK is greatly acknowledged for his support and for supplying the Celcure CCA-C 50% solution and the EN113 test specimens for the present investigation. Laboratory Technician Ebba Schnell is acknowledged for the careful and thorough experimental work.

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# The influence of oxalic acid on the bending strength of pinewood

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Afløsningsopgave for kursus 59204: Træteknologi*

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## Abstract

When Electrodialytic Remediation (EDR) is used for the removal of CCA from waste wood, oxalic acid has been used in many cases to facilitate the removal process. A total removal of CCA from wood would make it possible to either burn the remediated wood or perhaps otherwise reuse it. If the wood is to be reused the influence of oxalic acid on the wood strength must be investigated first. In this paper the influence on the bending strength of pine wood is investigated. Wood was treated with oxalic acid in three concentrations (30 mM, 300 mM and 1 M) and the bending strength was compared in washed and unwashed samples and in samples that was subjected to EDR. Samples treated with water served as a reference. The bending strength was measured with an INSTRON testing machine and a total of 104 samples were measured. The results showed that there was no significant difference in bending strength between oxalic acid treated samples and the reference. The results do not indicate that strength of wood is weakened by the use or presence of oxalic acid or as a consequence of EDR.

## Introduction

### CCA

Waterborne salts have been used to preserve wood for many years. One of the most common formulations contains copper, chromium and arsenic salts and is known as CCA (Chromated Copper Arsenate). During the impregnation of the wood, the CCA will be fixed in the wood matrix, either by precipitation or directly bound to the functional groups of the wood. This fixation is so strong that substantial amounts of CCA will remain in the wood for many years. Average life span of CCA-treated wood is

normally estimated to be 20-40 years. When CCA-treated wood is removed from service, the CCA contents makes an environmentally save disposal of the wood necessary. This is especially true since large quantities of wood are removed for aesthetic reasons rather than rot or bug attack. (e.g. *McQueen & Stevens 1998*)

## Legislation

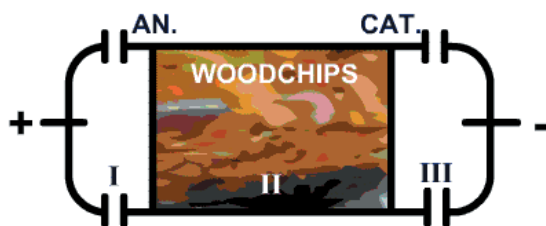
In Denmark, the use of CCA was banned in 1993, when Arsenic was prohibited for use in wood preservation. But due to the long life span of the wood, the waste problem will consist in years to come. The Danish EPA (Miljøstyrelsen) have estimated that approximately 2.7 million ton of treated wood has been used (accumulated) in Denmark since 1960. The amount of wood to be disposed is expected to increase from 17,000 tons in 1992 to 100,000 in 2010. (*Affald 21*)

Incineration of CCA-treated wood is prohibited in Denmark. This is due to the heavy metals still in the wood. By incineration the metals are being accumulated in the residues, creating a highly toxic waste product. Instead all treated waste wood should be placed in landfills until new methods have been introduced that ensures reuse of the wood resources (energy and metals).

## Electrodialytic Remediation

Electrodialytic Remediation is a method developed by researchers at the Technical University of Denmark (DTU), for cleaning soils polluted with heavy metals. Good results have been obtained using this method on soil, and subsequently the method has been tested on other materials e.g. fly ash, sludge and most recently CCA-treated waste wood.

The method uses a direct electric current as cleaning agent and combines it with the use of ion exchange membranes to separate electrolytes and soil. Figure 1 shows the electrodialytic cell in principle. Additional information on the Electrodialytic method is presented elsewhere (*Hansen et al. 1999; Ottosen et al 1997*)



**Figure 1:** Schematic presentation of an electrodialytic cell. Compartment I and III are the anode and cathode compartment respectively, compartment II contains the wood chips. AN: anionic exchange membrane. CAT: Cationic exchange membrane.

Prior to the remediation experiments, the wood chips are added oxalic acid. The oxalic acid serves two purposes, it ensures electric conductivity and it facilitates the removal of CCA from the wood by keeping pH low and acting as a complexing agent for copper and chromium.

By using electro-dialytic remediation, copper, chromium and arsenic will be removed from the wood (compartment II) and accumulated in the electrolytes (I and III). The metals collected in the electrolytes are proposed reused in the preservation industry after some adjustments.

As the wood chips no longer contains copper, chromium and arsenic, the wood may be burned and thereby the energy source will be utilized.

If the wood is to be used in another way, the influence by oxalic acid on the wood must be investigated first. The objective of this report is to investigate the influence of oxalic acid on the wood strength. The parameter chosen for this investigation is bending strength, because the measurements are simple and altering of tensile strength (which is supposed to be most affected) will be reflected in the results. This investigation should be looked upon as preliminary. Further investigations are to be made if the results from this report show any influence by oxalic acid on the bending strength of wood.

## Role of Oxalic acid

Apart from being used for remediation of CCA-treated wood, oxalic acid also plays a role in wood decay. (*Shimada et al. 1997; Micales 1997; Connolly, 1996*)

Both brown-rot and white-rot decay processes involves the production of oxalic acid. Wood-rotting fungi contains two oxalate producing enzymes (oxaloacetase and glyoxylate oxidase) and the oxalate metabolism may play a key role in transforming excess wood carbon into CO<sub>2</sub>.

During brown-rot decay process, oxalic acid may serve as a proton donor or an iron chelator for breaking wood carbohydrates. It has been reported that brown-rot fungi produce large amounts of oxalic acid, which accumulates in the cultures. During white-rod decay processes no accumulation is taking place. (*Shimada et al. 1997*)

Also the ability of oxalic acid to form stable complexes with copper has an influence on some fungi's ability to attack copper preserved wood. (*Clausen, C.A. et al. 2000*)

By investigating the influence of oxalic acid on wood strength, and by using 3 different concentrations of oxalic acid, information's will be available on the influence of oxalic acid caused by decay (low concentration) and by remediation (medium concentration). Finally the strength is tested after exposing the wood to an unrealistically high concentration (saturated oxalic acid solution).

## Experimental conditions

### Wood

104 samples of pinewood with the dimensions: 8x20x155 mm (64 samples) and 8x20x160 mm (40 samples) were used in this experiment. The wood was distributed into 8 equal groups. The intention was to ensure equal variation between and inside each group. Distributing the samples in a way that no group contained two samples that had been placed adjacent in the wood from where the samples came was part of the solution.

### Groups

Each group represents a different treatment of the wood. In table 1 the experimental conditions for each group is shown. The samples were pre-treated with different concentrations of oxalic acid according to the table. This was done using vacuum preservation. The samples were placed in the liquid and the air was removed by pumping (30 Mbar). When no more air escaped the samples, vacuum was released and the samples were thereby saturated with the liquid. The samples in group 3 was subsequently placed in an electrodynamic cell and exposed to direct electric current for 72 hours. The current was kept constant at 40 mA and the voltage drop was at no time higher than 10 V. The treatment was the same as normally used when removing heavy metals from CCA-treated waste wood. The objective of this treatment was to examine if the electrodynamic remediation process had any influence on the strength of the wood. During the experiment the samples from the other groups were kept in closed containers, in the liquids used in the vacuum preservation.

**Table 1:** Experimental conditions for the 8 groups.

Group	[Oxalic acid]	Additional treatment
1	300 mM	Washed
2	300 mM	
3	300 mM	Electrodynamic remediation
4	1 M	Washed
5	1 M	
6	30 mM	Washed
7	30 mM	
8	0	

The samples in group 1, 4 and 6 were “washed” 3 days after the vacuum preservation in order to extract the oxalic acid before the bending strength experiments. Ideally this would be done using vacuum preservation with water instead of oxalic acid, to ensure

that the water reached all parts of the wood, but do to limited time, this was only done with group 4 (the highest concentration). Prior to that the samples from all 3 groups had been “washed” by soaking the samples in distilled water for app. 8 hours. This was repeated 5 times.

By comparing the results of the washed and the unwashed, it was hoped that the results could reflect whether an eventual weakening of the wood exposed to oxalic acid was due to the oxalic acid crystals itself or if the oxalic acid had attacked and damaged the wood chemically.

The samples were subsequently conditioned according to standard by placing the wood in a room with constant temperature and humidity ( $20 \pm 2$  °C and  $65 \pm 3$  % relative humidity). After 10 days a random check was done and it was found that the samples were in equilibrium – as the weight of the samples didn’t change more than 0.1 % in 24 hours.

Before the tests started all the samples were weighed (to two decimals) and the dimensions measured using Vernier Gauge. In all samples the variations in dimensions were within acceptable range.

Bending strength was measured with an INSTRON testing machine. Experiments were done according to standard: SKANORM 7, Determination of ultimate strength in static bending. The norm is in agreement with ISO 3133 (1975).

In the bending strength experiments, the sample was placed symmetrically in the apparatus, with a span ( $l$ ) of 120 mm. This equals the heighth ( $h$ ) (tangential plane) times 15. The load was applied on the radial plane of the sample ( $b$ ), with constant speed.

The time span until “bending failure” should be between 60 and 120 seconds.

The bending strength are calculated according to the equation below,

$$\sigma_{b\omega} = \frac{3 \cdot F_{\max} \cdot l}{2 \cdot b \cdot h}$$

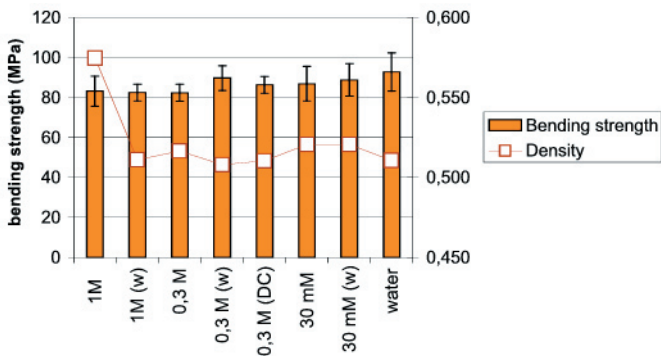
And adjusted to 12 % moisture content by:

$$\sigma_{b12} = \sigma_{b\omega}(1 + \alpha(\omega - 12)) \quad (\alpha = 0,04)$$

## Results

All data are presented in appendix 2.

The results are illustrated in figure 2.



**Figure 2:** Bending strength (mean value  $\pm$  95% CL) and mean density, illustrated for the different treatments. The results are adjusted to 12% moisture content.

With the results obtained in this experiment, no significant difference in bending strength due to oxalic acid or electrochemical remediation can be concluded. For all 8 groups there is an overlap of confidence limits.

The density for the samples treated with 1 M oxalic acid (and not washed) differs from the other samples. This is possible due to the oxalic acid crystals present in the wood samples, and seems to have no influence on the strength of the wood.

## Exclusion of results

Prior to the statistical analysis, two results were excluded. This was done because time to failure of the sample was either too short (42 sec.) or too long (>400 sec.). The samples were from group 7 and 8 respectively.

For the remaining 102 samples, the time to failure was between 61 and 132 sec. Five samples failed above the recommended 120 sec. These are not rejected, as it is estimated that the deviation from the recommended is negligible.

A Q-test on the remaining 102 results made no further exclusion possible.

## Conclusion

In this experiment no significant difference in bending strength was observed between samples treated with oxalic acid and control samples. Furthermore the Electrochemical Remediation process doesn't seem to have any influence on the bending strength. The results from this experiment do not indicate that the strength of the wood is weakened by the use (content) of oxalic acid. In the situation where oxalic acid is present due to decay of the wood, there will of course be a reduction in the strength of the wood, due to decay, but no additional weakening due to oxalic acid is likely to occur.



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# Distribution of copper and chromium in partly remediated CCA-treated wood

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## Abstract

When electrodialytic remediation or batch extractions by soaking in different acids have been used for removing CCA from waste wood, promising results have been obtained, although 100% removal of the metals were not achieved.

In this work, EN 113 test specimens were treated with CCA. Afterwards samples of the wood were subjected to soaking and electrodialytic remediation.

SEM/EDX analyses of the wood both prior to and after remediation were carried out in order to give information regarding the distribution of the metals in the wood.

Based on the SEM-EDX analysis performed and the microstructural observations by SEM there was a distinct difference in the distribution of Cu and Cr before and after subjection of test specimens to extraction by acid and electrodialytic remediation. Before soaking the Cu and Cr seemed to be mainly incorporated into the cell walls and no visible deposits of the metals were found in the tested samples. Afterwards the metals were still present in the “background”, i.e. cell walls without visible deposits, but also visible deposits of the two metals were detected. The Cr seemed to be predominantly deposited in connection with the rays, while Cu was mainly found in deposits on the lumen surface of tracheid walls. Total removal of Cu and Cr was not obtained, but the concentration of both metals could be reduced significantly by soaking and electrodialytic remediation. When examining the SEM/EDX analyses, the reduction was mainly visible for Cu in the tracheids.

## Keywords:

Chromium, Copper, Electrodialytic remediation, SEM/EDX

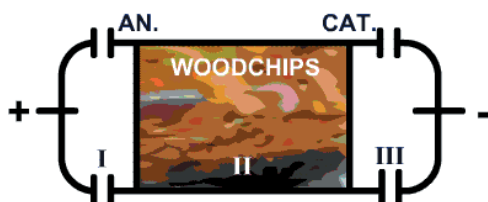
## Introduction

### Waste Wood

When wood treated with Chromated Copper Arsenate (CCA) is removed from service, the content of copper (Cu), chromium (Cr) and arsenic (As) is still high in many cases (*Cooper et al. 2000*) and even though the use of CCA-treated wood has been reduced by regulation in recent years, both in Europe and in USA, the estimated service life of 25-50 years for CCA-treated wood (*Syrjänen 1999*) makes handling of CCA-treated waste wood necessary for many years to come. Therefore a method for safe handling of waste wood and reuse of wood resources would be environmentally beneficial

### Electrodialytic Remediation

Electrodialytic remediation (EDR) is a method originally developed for removing heavy metals from polluted soils, and has subsequently been used for remediation of other materials, including CCA-treated waste wood. In EDR an electric field is applied to the wood, causing the ions in the wood – including Cu, Cr and As ions from CCA – to move toward the electrodes, according to their charge. In figure 1, the electrodialytic setup is shown in principle. Wood chips are placed in the middle compartment (II) and covered with a liquid to ensure electric conductivity and in some cases to facilitate mobilisation of the metals. The liquid is typically an acid or water. The electrodes are placed in compartment (I) and (III), where a weak electrolyte solution circulates. The electrodes are separated from the wood by means of ion exchange membranes. The ions will move from the middle compartment into the liquids in compartment (I) and (III), from where they can be recovered. The method is developed and patented at the Technical University of Denmark, and is described in more detail by *Hansen et al. (1999)* and *Ottosen et al. (1997)*.



**Figure 1:** Schematic presentation of the electrodialytic remediation setup. Compartment (I) and (III) contains the electrodes, compartment (II) contains the wood chips.

AN: anion exchange membrane, CAT: cation exchange membrane

The first EDR experiments on CCA-treated wood were performed by A. Ribeiro. The results were very promising with 93% Cu, 95% Cr and more than 99% As removed in a 30 days experiment (*Ribeiro et al. 2000*). Ribeiro used CCA-treated waste wood in the form of sawdust and the best results were obtained with 2.5% oxalic acid as an additive in the middle compartment.

In the following research at the Technical University of Denmark, the possibility of remediating wood chips instead of sawdust was investigated. The use of a larger wood fraction than sawdust results in lesser processing of the treated wood and lower expenses. By reducing the processing of CCA-treated wood, the workers doing the processing is not exposed to airborne particles to the same degree, and a safer work environment is created.

In the laboratory app. 95% Cu and 85% of both Cr and As was removed from CCA-treated waste wood chips at the end of a 7 days experiment (*Kristensen et al 2001*). Oxalic acid was used as an additive during the remediation. In larger scale experiments (2 m<sup>3</sup>) similar results have been obtained (*Pedersen et al. 2004, Christensen et al. 2004*), whereby app. 88% Cu, 82% Cr and 96% As was removed after 21 days of remediation. In the larger scale experiment it proved to be more suitable to soak the wood in the additive prior to the remediation and use water in the middle compartment during remediation. The best results were obtained by dual soaking. First, the wood was soaked in phosphoric acid and then in oxalic acid.

## Aim of the Present Paper

Even though good results have been obtained in removing Cu, Cr and As from CCA-treated wood, both in the laboratory and in larger scale experiments, it has not been possible to remove 100% of the metals. In this investigation, the aim is to examine the distribution of CCA in the wood using the SEM/EDX technique on specimens, prior to and after remediation to see if there is evidence of a certain type of wood-metal bonding that is not affected by electrodialytic remediation, or if the metals seem evenly removed from all parts of the wood. The investigation may contribute to an explanation to why a total removal of CCA from waste wood has not been obtained so far.

The main focus of this investigation is on Cu and Cr, because the SEM/EDX signal (peak) of As is close to the signal of Au routinely used for sample coating. In most cases it is impossible to separate the two signals and therefore As will only be evaluated in a few of the analyses that is presented here.

## Experimental Section

### Impregnation of Test Specimens

EN113 test specimens (50 mm x 25 mm x 15 mm) were used instead of the treated

waste wood chips normally used for EDR. The reason for this is that it will be easier to compare the experiments when the same wood and CCA-treatment has been used, instead of waste wood chips, where both wood species, CCA type and CCA loading may differ.

The test specimens were impregnated with a solution containing 2% Celcure CCA-C. The wood preservative was obtained from Osmose, DK. The impregnation was made in a vacuum desiccator. After placing the test specimens in the desiccator and adding sufficient volume of the treating solution, vacuum was applied corresponding to a pressure of 4kPa. The vacuum was maintained for 20 min and the test specimens were left in the CCA solution for 2 hours. Afterwards the test specimens were removed from the solution and placed in a condition chamber ( $20 \pm 2^\circ\text{C}$ ,  $65 \pm 5\%$  relative humidity) for 14 days. For the first week they were kept in sealed black plastic bags to ensure fixation of CCA.

The impregnation took place approx. one month prior to the extraction and electro-dialytic remediation experiments.

## Remediation Experiments

The test specimens was subjected to similar experimental conditions that had produced the best and most interesting results with CCA-treated waste wood so far. (Kristensen et al. 2001, Pedersen et al 2004, Christensen et al. 2004) Oxalic acid was the most used additive and therefore test specimens were investigated after soaking in oxalic acid. These results were compared with an experiment where soaking was followed by EDR. By comparing the two experiments, the influence of the electric current on the remediation and distribution of Cu and Cr was evaluated. In larger scale (2 m<sup>3</sup>) the best results were obtained using dual soaking with phosphoric acid and oxalic acid prior to remediation. In the laboratory it was found that the order of soaking had a great influence on the remediation especially of Cu. For this purpose two soaking experiments were compared differing in the order of applied soaking solutions. Again the influence of the electric current on the remediation was evaluated by comparing the dual soaking experiment that results in the highest removal of Cu and Cr with an experiment where the soaking was followed by EDR

In table 1 the experimental conditions for the experiments are shown.



**Table 1:** Experimental conditions for exp. 1-6. Exp. 1 (reference) is impregnated test specimens prior to any remediation. \*5% oxalic acid corresponds to approx. 0.66 M oxalic acid

Experiment	Soaking 1/ duration	Soaking 2/ duration	Current/ duration	Additive
1 (reference)				
2	*5% oxalic acid/24h			
3	*5% oxalic acid/24h		5 mA/3 days	2,5% oxalic acid
4	0,5 M oxalic acid /18h	0,5 M phosphoric acid/18h		
5	0,5 M phosphoric acid/18h	0,5 M oxalic acid /18h		
6	0,5 M phosphoric acid/18h	0,5 M oxalic acid /18h	30 mA/4 days	Tap water

Impregnated test specimens prior to any remediation (exp. 1) were used as a reference for the other experiments.

In experiment 2, the test specimens was soaked in oxalic acid for 24 hours. In exp. 3 the soaking was identical to exp. 2, but in addition the wood was subjected to EDR for three days with oxalic acid as an additive. In exp. 4 and 5 dual soaking was performed. In exp. 4 the test specimens were soaked in oxalic acid, followed by soaking in phosphoric acid. In exp. 5 the soaking procedure was vice versa. In exp.6 EDR was applied to the wood for 4 days after dual soaking similar to exp. 5.

## AAS

After remediation according to table 1, the concentrations of Cu and Cr were measured with Atomic Absorption Spectroscopy (AAS) after microwave-assisted acid digestion of three samples of wood in all experiments. Each sample weighted 0.25 g and was digested in 10.0 ml of concentrated nitric acid. Prior to AAS measurement the sample was diluted to a final volume of 25.0 ml with distilled water.

The results are shown in table 2.

## SEM/EDX

The SEM/EDX analyses were made using a Hitachi S-520 SEM at an accelerating voltage of 15 kV. The SEM was equipped with a Kevex 7100 EDX system. The samples were cut and oriented to disclose the radial section and Au-coated prior to the analysis. A series of point and scan analysis were made using the SEM/EDX system and the interpretation of the results were based on these findings.

Results and Discussion

AAS analyses

In table 2 the concentrations of Cu and Cr in the wood for the six experiments are shown.

Table 2: Content of Cu and Cr in the wood as a mean of 3 measurements

Experiment	Cu [mg/kg]	Cr [mg/kg]
1 (reference)	3195	8656
2	3190	6693
3	2314	1161
4	3144	1617
5	934	1232
6	379	1230

Experiment 1 gives the initial concentration of CCA in the wood. In the other experiments, the wood has been subjected to extraction by soaking in acid and in exp. 3 and 6 electrodynamic remediation was additionally applied. The purpose of the treatment was to reduce the concentration of Cu and Cr in the wood. For Cr this was achieved in all experiments and the concentration was reduced to between 13% and 77% of the initial concentration. The highest removal of Cr was measured in exp. 3, where the wood was soaked in oxalic acid, followed by EDR. For Cu there was a significant reduction in all but two experiments (exp. 2 and 4). The lack of remediation coincides with the use of oxalic acid for soaking, probably because Cu could form CuOx precipitates with oxalic acid, which are only slightly soluble in water. In exp. 3 the soaking in oxalic acid was followed by EDR leading to a reduction of the Cu concentration to app. 72% of the initial. In exp. 4, where the soaking in oxalic acid was followed by soaking in phosphoric acid, the removal of Cu was negligible. An explanation for this could be that CuOx precipitates do not dissolve in the presence of phosphoric acid. Instead more CuOx precipitates may be formed. The acid dissociation constants for the two acids are shown in table 3 and indicate that the equilibrium may be shifted towards higher dissociation of oxalic acid when phosphoric acid is present.

Table 3: pKa values for oxalic- and phosphoric acid (*CRC Handbook of Chemistry and Physics*, 73rd ed. 1992)

pKa	Oxalic acid	Phosphoric acid
1	1.23	2.12
2	4.19	7.21
3	-	12.67

The mechanism may be that when the treated wood is initially soaked in oxalic acid, a part of the fixed Cu ions in the wood are replaced by protons from oxalic acid. The Cu ions may then precipitate as CuOx on or inside the wood. After a period of soaking, the wood is removed from the oxalic acid solution and placed in phosphoric acid instead. At this point the cell lumens would already contain oxalic acid, and when phosphoric acid is added in excess during the second soaking, the dissociation constant of the two acids would favour dissociation of oxalic acid and subsequently more CuOx would be formed instead of dissolved.

Theoretically it is also possible that Cu could precipitate with phosphate ( $\text{Cu}_3(\text{PO}_4)_2$ ). A combination of the different precipitates could also be possible.

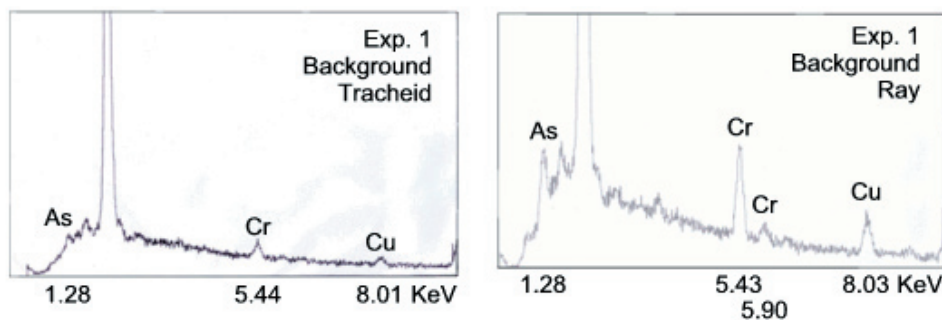
When the order of soaking was reversed (exp. 5), the removal of Cu was drastically improved with less than 30% left in the wood. The improved Cu extraction when the order of soaking was reversed could be due to ion exchange. Cu ions are not precipitated, but removed with the phosphoric acid when the liquid phase was changed from phosphoric to oxalic acid.

In exp. 6 the dual soaking from exp. 5 was followed by EDR resulting in optimum remediation. The concentration of Cu was reduced to app. 12% of the initial concentration. When comparing exp. 2 to exp. 3 and exp. 5 to exp. 6, the effectiveness of EDR application may be evaluated. In both EDR experiments there was a higher removal of Cu compared to the experiment with only soaking. For Cr the effect of EDR could be seen when comparing exp. 2 and 3, but in the dual soaking experiments (exp. 5 and 6), the effect of EDR on the Cr removal could not be seen. This was however the case in other remediation experiments using chipped waste wood, where a total of 82% Cr was removed after remediation. After the dual soaking 56% of the Cr was removed and the remaining 26% was removed during EDR (*Pedersen et al 2004, Christensen et al. 2004*). The removal of Cu and Cr from CCA-treated wood is shown improved by EDR compared to extraction by soaking alone, based on the results obtained in previous and present papers.

## SEM/EDX analyses

### Experiment 1 – CCA treated wood

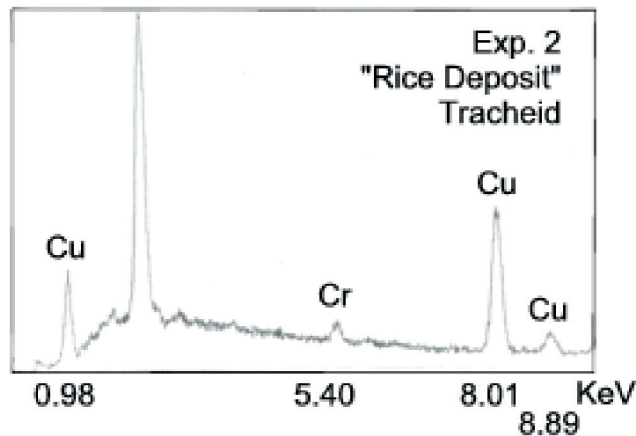
In this sample no visible precipitations/deposits were found, but SEM/EDX analyses confirmed that Cu and Cr (and As) was still present both in tracheids and in rays (figure 2). No difference in the Cu : Cr : As ratio was found between rays and tracheids. The metals were detected in areas without apparent deposits.



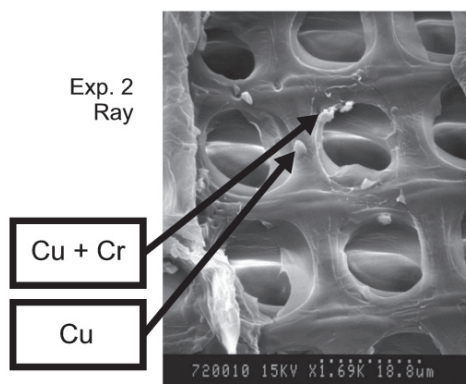
**Figure 2:** SEM/EDX analyses in exp. 1 (reference). Background in tracheid and ray.

## Experiment 2 – oxalic acid soaking

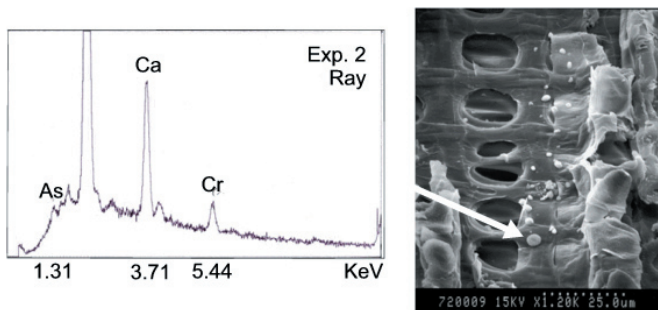
Rice shaped deposits were found in the tracheids. They contained Cu and only small amounts of Cr. In figure 3 a SEM/EDX analysis of a “rice deposit” is shown. Other types of deposits were found along cross field pittings. Figure 4 is a SEM picture with distinct deposits both on the edge of the window pit and on the cell wall between the pits. Based on SEM/EDX analyses (results not shown) it was found that some deposits contained both Cu and Cr, while others only contained Cu. Another deposit, also found along rays contained primarily Ca (calcium) and Cr (see figure 5). No Cu was present in the deposit, but whether or not As was present is open for interpretation, since the signal for As was partly covered by the Au signal.



**Figure 3:** SEM/EDX analysis of a rice shaped deposit found in the tracheids in exp. 2 (oxalic acid soaking)



**Figure 4:** SEM picture showing deposits in connection with ray cells in exp. 2 (oxalic acid soaking). The localisation of deposits containing Cu and Cr are based on SEM/EDX analyses, results not shown.

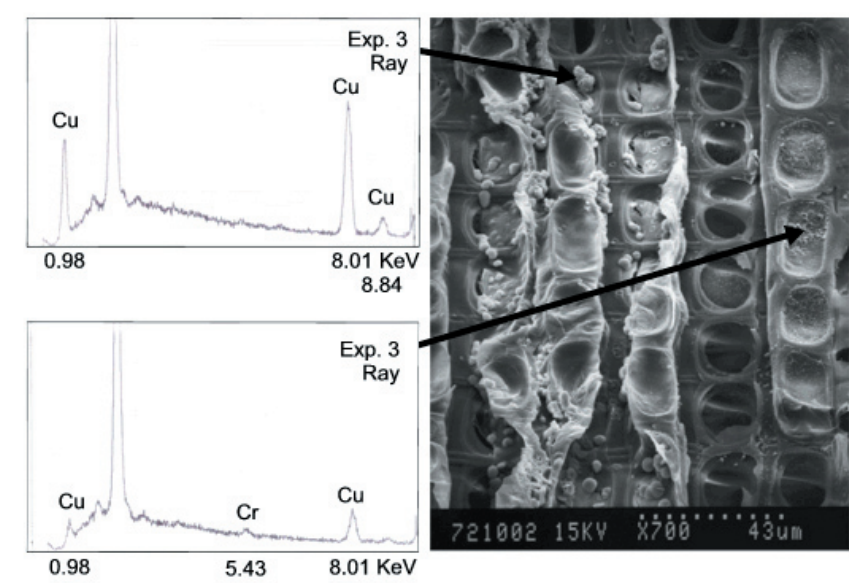


**Figure 5:** SEM/EDX analysis of a deposit found in connection with the ray cells in exp. 2 (oxalic acid soaking)

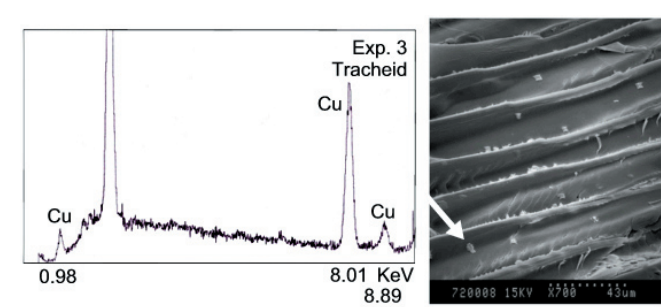
### Experiment 3 – oxalic acid soaking, followed by EDR

Large deposits containing Cu were located along the rays, where also smaller deposits were found to contain both Cu and to a lesser degree Cr (see figure 6).

Figure 7 is a SEM/EDX analysis of the deposits found in the tracheids. The deposits were square-like in shape and contained Cu, but not Cr.



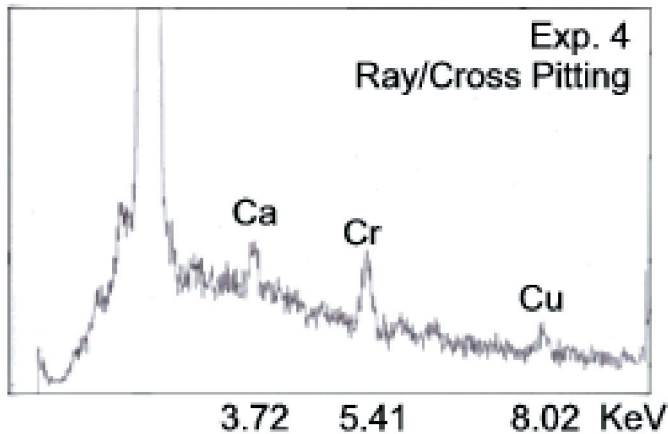
**Figure 6:** SEM/EDX analyses of deposits found along ray cells in exp. 3 (oxalic acid soaking, followed by EDR)



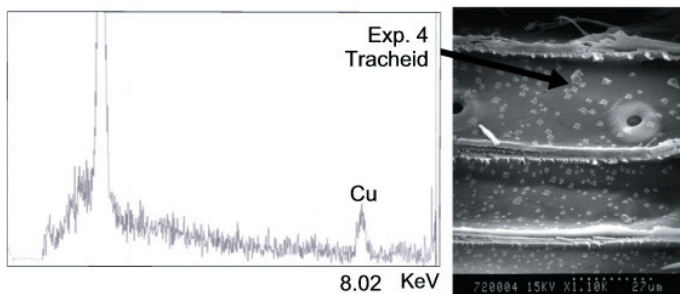
**Figure 7:** SEM/EDX analysis of deposits in tracheids of exp. 3 (oxalic acid soaking, followed by EDR)

**Experiment 4 – dual soaking (oxalic, phosphoric)**

Deposits containing Cu, Cr and Ca were found at cross field pittings (see figure 8). Figure 9 shows deposits found within tracheids. The square-like deposits contained Cu, but no Cr.



**Figure 8:** SEM/EDX analysis of deposits found at cross field pittings of wood from exp. 4 (dual soaking: oxalic acid, phosphoric acid)

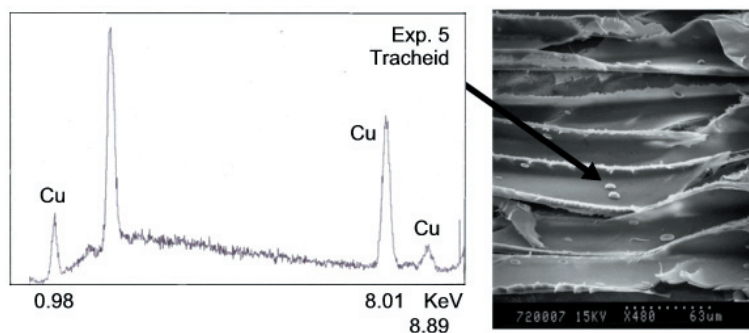


**Figure 9:** SEM/EDX analysis of deposit in tracheids of wood from exp. 4 (dual soaking: oxalic acid, phosphoric acid)

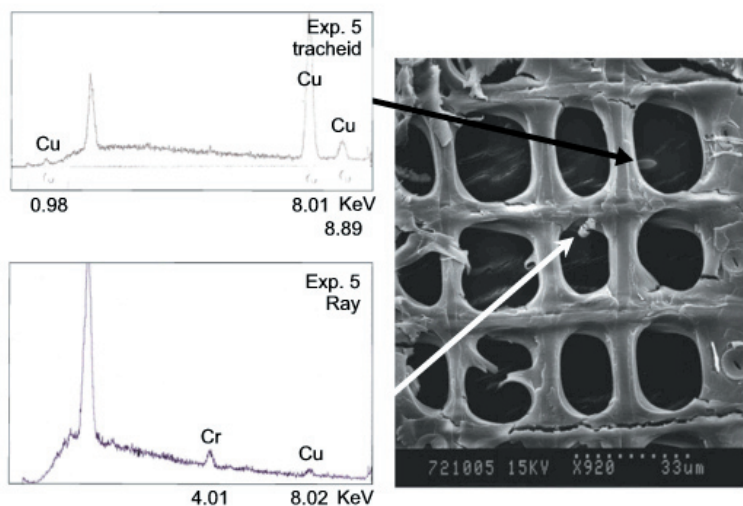
## Experiment 5 – dual soaking (phosphoric, oxalic)

The deposits that were located in the tracheids are shown in figure 10. The deposits contained only Cu and were rice-shaped. Deposits containing Cu and Cr were found on the edge of a ray window. In the underlying tracheids Cu-containing deposits were found. (see figure 11)





**Figure 10:** SEM/EDX analysis of deposit in tracheids in exp. 5 (dual soaking: phosphoric acid, oxalic acid)

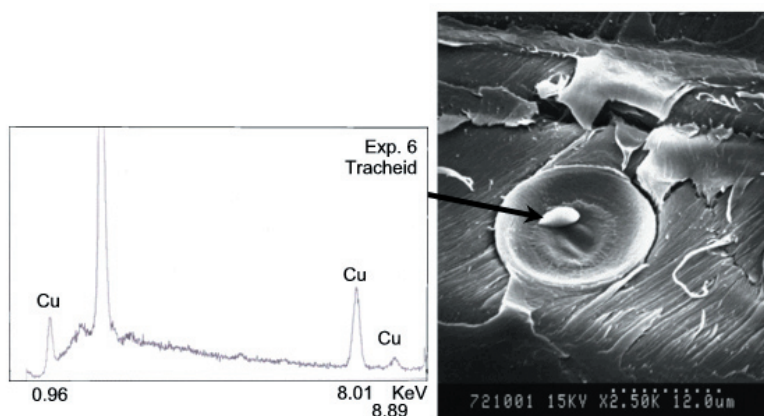


**Figure 11:** SEM/EDX analysis of deposit found along cross field pittings (tracheids and ray) in exp. 5 (dual soaking: phosphoric acid, oxalic acid)

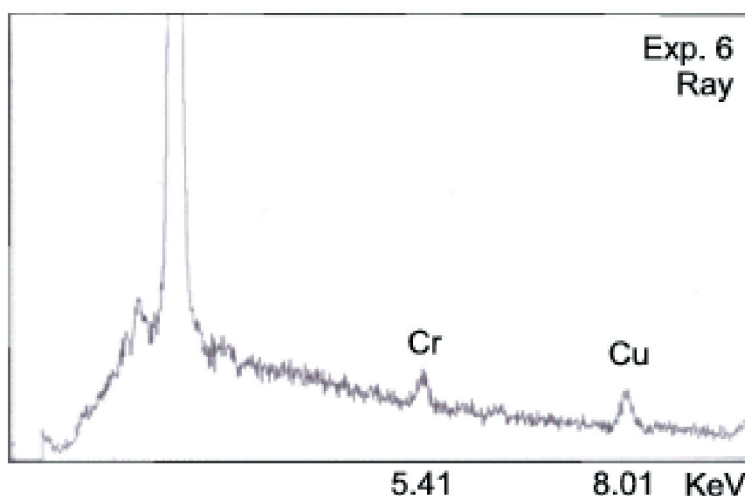
### Experiment 6 – dual soaking (phosphoric, oxalic) followed by EDR

Only few Cu-containing deposits were found in the tracheids, in figure 12 a rice-shaped deposit is shown. The deposit was found on a pit membrane and contained Cu but no Cr. Deposits containing both Cu and Cr were found in ray cells (figure 13)





**Figure 12:** SEM/EDX analysis of deposit found on a pit membrane in wood from exp. 6 (dual soaking: phosphoric acid, oxalic acid, followed by EDR)



**Figure 13:** SEM/EDX analysis of deposit found in a ray cell of wood from exp. 6 (dual soaking: phosphoric acid, oxalic acid, followed by EDR)

## Comparison and discussion of SEM/EDX results

In the CCA treated wood specimens Cu, Cr and As was found in similar ratios in both rays and tracheids. The metals seemed to be incorporated in the cell walls rather than deposited on the surface, since no visible deposits were found during the SEM/EDX investigations. In SEM investigations performed by *Greaves (1974)* amorphous and crystalline deposits were found in every SEM examination of unleached softwood. The deposits were found in ray cells and consisted probably of water soluble combi-

nations of Cu, Cr and As. No definitive answer can be offered as to why these deposits were not found in the reference test specimens of the present investigation, but it is not possible to exclude the possibility that deposits were present but not detected. Another explanation may be that the magnification was not sufficient in this SEM/EDX investigation (X3000) to see the deposits. Chou et al. (1973) found that even though the cell lumen surface appeared to be “clean” at low magnification, a thin layer of CCA that covered the surface could be detected at higher magnification (X99000 – 171000).

After the test specimens were soaked in oxalic acid (exp. 2), deposits were located in both the ray cells and the tracheids. In addition to Cu and Cr, one deposit also contained Ca. This is in agreement with *Bailey et al (1996)*, who found enriched concentrations of e.g. Ca in the ray parenchyma wall. According to table 2 the concentration of Cu in exp. 2 remained unchanged but Cr was reduced to app. 77% compared to the reference. It is not possible to compare the SEM/EDX analyses for the two experiments, since the Cr was not visible in exp. 1, but at least some of the Cr was present as visible deposits in exp. 2.

In exp. 3 the soaking in oxalic acid was followed by EDR. Here, the concentrations of both Cu and Cr were reduced when compared with exp. 2, implying that both metals could be removed from the wood by EDR. Cr was found in only some of the deposits along the rays, and not in the tracheids. The reduction of Cu was not obvious when comparing the analyses of the two experiments, but the Cu deposits found in the tracheids seemingly changed shape from rice-like after soaking in exp. 2 to square-like after EDR in exp. 3

In exp. 4 and 5, where the test specimens were subjected to dual soaking – but in reverse order, the difference in Cu concentration was obvious both when total concentrations were measured and when SEM/EDX analyses were compared. The difference was profound when the tracheids were analysed (see. Figure 9 and 10). When the test specimens were soaked in oxalic acid, before phosphoric acid (exp. 4), the Cu was not removed and could be found as square-shaped deposits in the tracheids. When the reverse soaking order was applied (exp. 5) 70% of Cu was removed and the abundance of Cu deposits in the tracheids was greatly reduced compared to exp. 4. The shape of the deposits was rice-like instead of square-like. In exp. 6, where the dual soaking from exp. 5 was followed by EDR, only few deposits was found in the tracheids and with similar rice-like shape as found after soaking. The difference in Cu deposits in the tracheids was very distinct. It has been argued earlier in this paper that the square-like deposits in exp. 4 are CuOx. The same type of deposits was also found in exp. 3 where the wood was soaked in oxalic acid, followed by EDR. The rice-like deposits were found in exp. 2, 5 and 6. In exp. 5 and 6 it might be possible that the deposits did not contain oxalic acid, since the test specimens was also soaked in phosphoric acid, and in exp. 6 also EDR was applied. In exp. 2 however, the wood specimens was soaked only in oxalic acid and it is likely that the Cu-containing deposits found here would be CuOx, and these deposits are rice-like. Thus it is possible that both rice-like and square-like deposits contain CuOx.

In general Cu deposits were found both in tracheids and in connection with rays. Cr deposits were almost exclusively found in connection with the rays. Even though the rays are considered the main route for the CCA solution to enter the wood in industrial wood preservation (*e.g. Greaves 1974*), this was probably not the case in this investigation. Since the flow in the longitude direction is considered to be much faster than the flow in the radial direction and the dimension of the EN113 test specimens are 50 mm longitude and 25 mm, the dimension of the test specimens would favour uptake in the longitude direction.

The pattern of Cr dominating in the rays were in agreement with the findings of *Yamamoto et al. (1989)*, who estimated the concentration of Cr in CCA treated wood to be app. 1.6 higher in the ray parenchyma cell walls compared to the tracheid walls. The tendency of higher metal content in rays are attributed to the fact that the wall structure of ray parenchyma cells is quite different from that of tracheids and that probably causes differences in chemical composition and wall porosity. Cu and Cr were found in the background in all experiments and both in ray cells and tracheids. In addition to that, deposits were found in all the experiments where the wood specimens had been subjected to treatment. It seems that when the reduction of Cu and Cr was profound, it was reflected in the abundance of deposits. This was especially true for Cu in the tracheids, but it is not possible to establish if the measured removal of Cu (in table 2) were due to removal of Cu in visible deposits, or if there has been removal of Cu from the “background” as well.

It seems possible that the rice-like deposits found in exp. 6 after dual soaking and EDR could be removed with further remediation, since the same type of deposits were found to decrease in abundance after dual soaking (exp. 5) and even further after EDR (exp.6). However it is not possible based on these investigations to determine if the CCA still present in the background after soaking and EDR, can be removed after further remediation or if it will remain in the wood.

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# 7 Electrodialytic remediation of waste products

- Based on results and experiences obtained in the process of optimising the EDR method to remediation of CCA-treated waste wood

## 1. Introduction

The electrodialytic remediation method (EDR) has the possibility of being used for remediation of a variety of waste fractions. The method was originally developed for removal of heavy metals from soil but has subsequently been used for removal of heavy metals from other materials too – e.g. CCA-treated waste wood.

When the EDR method is transferred to a new waste product, it is necessary to optimise the method to some degree to fit the purpose. This was also the case when CCA-treated wood was to be remediated.

In the present paper the experiences regarding optimisation of EDR during the work with CCA-treated waste wood are presented with the intention that it may be useful in future optimisations of EDR to remediate other materials.

## 2. Type of pollution

The EDR method may in principle be used for the removal of both organic and inorganic pollutions but has predominantly been used for removing heavy metals from a waste fraction.

In order for the heavy metals to be removed by electro migration, they have to be present in the form of ions during EDR. Therefore it is essential that the pollution is either present as ions or it can become ionic with a minimum of effort.

Often knowledge of the origin of the pollution is available and thereby information regarding the form (metallic or ionic) of the heavy metals can be obtained.

In the case of CCA-treated wood, Cu, Cr and As is in the form of ions either fixed to the wood substances or precipitated on the (inner) surfaces of wood cells.

In the cases where no information is available on the form of the heavy metals, knowledge may be obtained by experimental investigations, such as extraction experiments. (see section 4.1)

### 3. Polluted material

The polluted material may be liquid (e.g. waste water) or solid (e.g. soil).

In order for the current to be able to remove the ions from the inside of a solid material, some kind of porosity is needed to moisten the material and allow the ions to move.

A general observation regarding the suitability of polluted materials for EDR may be: If the heavy metals are present as ions, and were originally placed in (or on the surface of) the materials as ions, then this will be a good indication of the possibility to remove the heavy metals again.

#### 3.1 Size fraction

Size of the material needs to be considered. In the case of fly ash, the natural particle size is small and further procession to reduce the particle size is not relevant (*Pedersen 2002*). In soils and harbour sediments, heavy metals are found to be accumulated in the fine (clay) fraction (*Alloway 1995*). If this fraction is separated from the rest of the soil before EDR, a faster and more efficient removal of heavy metals may be obtained (*Ottosen 2004*). The separation of the fine fraction may be obtained by washing and sieving of the soil.

Waste wood may be present in the shape of poles or sawdust and thereby size reduction may be relevant and then it is necessary to consider the degree of reduction. Smaller particles mean a larger surface area from where the heavy metals can be removed. On the other hand it has to be considered that it is a material that contains often hazardous materials, e.g. like arsenic in CCA-treated wood, and that extensive processing will lead to workers being exposed to a high degree of airborne particles that may be hazardous.

In addition to that processing is also a financial factor that has to be taken into consideration.

Therefore processing should in general be kept to a minimum.

In the case of CCA-treated wood some kind of processing was essential in order to obtain a more uniform size distribution of the material. The remediation of different size wood chips was investigated as opposed to earlier experiments where sawdust was used. The results showed that it was possible to remove CCA from wood chips but also that the removal was easier at smaller size fractions. Higher remediation of the larger fractions could possibly be obtained by ensuring total saturation (penetration) of the larger wood size fractions. In wood this would require vacuum soaking of the wood prior to the remediation and this will also add to the total costs of the remediation.

## 4. Additive

In some cases it may be necessary to facilitate the removal of the heavy metals by using an additive. The additive may be an acid, since most heavy metal ions are more soluble at low pH and may precipitate at neutral or alkaline pH. Another possibility is to use an additive that may form complexes with the heavy metals, and remove the heavy metals as complexes. This may also make it possible to remove the heavy metals in alkaline conditions, if the formation of complexes prevents the heavy metals from precipitating. In alkaline materials and in materials with high buffering capacity, then it may be relevant to investigate remediation at high pH, and remove the heavy metals as complexes.

The additive should be chosen based on knowledge about the heavy metals to be removed and if possible the form of pollution.

In remediation of CCA-treated wood for instance, oxalic acid was initially tested, since reports showed that in some cases fungi that produced oxalic acid could decay CCA treated wood. This was attributed to the ability of oxalic acid to remove or detoxify the CCA components (*Eaton & Hale 1993*)

### 4.1 Extraction experiments

In the process of finding the most suitable additive a series of extraction experiments are often made, at different pH and concentrations of the additives. After extraction the percentage of heavy metal extracted is determined by measuring the concentration of the heavy metal in the liquid phase, compared to the initial amount in the material. Thereby the removal efficiency of different additives can be compared.

The removal results obtained by extractions can not be transferred directly to a removal efficiency to be expected in EDR since EDR provides a continuing removal of the heavy metal and thereby the equilibrium between the heavy metal in solution and heavy metal absorbed to the material may be moved towards further removal of the heavy metal.

It is important to realise that the fact that heavy metals can be extracted may not imply that the remediation by EDR is possible. In extraction experiments the heavy metal removal is determined based on the concentration of heavy metal in the liquid phase. It does however not distinguish between charged and uncharged species. For instance when a complex forming additive is used, the complexes formed with the heavy metals may have zero charge, and they will not be removed by the electric current, but stay in the middle compartment.

Extraction experiments can be used to compare the usability of different additive and concentrations of additives and may give a hint as to the optimum pH for the remediation process.



The optimal concentration of additive in the middle compartment during EDR depends on the ionization of the additive.

Ammonia ( $\text{NH}_3$ ) forms complexes with Cu and has been used for removal of Cu from soil at high pH. At high pH almost all ammonia is present as uncharged  $\text{NH}_3$  molecules and will not be removed from the middle compartment by ion migration.

In this case the concentration of additive in the middle compartment may be as high as possible to ensure high removal of the heavy metals.

In the case of the additive being present as ions (e.g. oxalate ions), the concentration of the additive in the middle compartment during EDR should be as low as possible in order to minimise the amount of current that is wasted by removing these non-target ions. This can be accomplished by using a low concentration of the additive directly in the middle compartment but most likely a part of the additive will be removed by the electric field before it comes into contact with the heavy metals to be removed. This leads to waste of additive and current and maybe even reduced removal of the heavy metals. Another possibility is soaking.

## 4.2 Soaking before use

Soaking is only considered an option in the case of easy separation of the solid material and the liquid phase. This is the case with wood chips, but in cases of fine grained (charged) materials like fly ash and soil, the separation will be too difficult since natural sedimentation of fine grained materials are slow and forced sedimentation by press or vacuum filtration is an expensive addition to the remediation process.

In remediation of CCA-treated wood the dry wood was soaked in the additive prior to EDR, and during EDR only water was used in the middle compartment. This proved to serve more than one purpose. The only additive that was present during EDR was already in the wood and thereby the amount of non target ions (additive ions) was reduced during EDR. In addition to that no current was used to remove the easily extracted ions, since this part was removed during soaking.

## 4.3 Remediation with no additive

In the remediation of fine particle materials, like soil and fly ash acid may be generated during the remediation as a consequence of water splitting at the anion exchange membrane (*Ottosen et al. 2000*). In these systems it may be more efficient to have the acid generated directly in the middle compartment during EDR instead of acidifying the material first.

The acidification during EDR does not take place to a measurable degree when CCA-treated wood is remediated. It has however been seen in the remediation of small charged particles like fly ash, and soil (*Ottosen et al. 1997, Pedersen 2002*) The reason



for this is not fully understood, but the formation of a thin particle layer on the anion exchange membrane that may turn areas of the membrane into a bipolar membrane may be one explanation.

## 5. EDR Set up

### 5.1 Three- or five-compartment set-up

When a suitable additive is identified the next step is EDR experiments in laboratory scale. The standard set-up consists of three compartments: a middle compartment with the polluted material and two electrode compartments and this may often be suitable for the remediation.

However in the cases where the heavy metals precipitate onto the electrodes, the five compartment set-up may be introduced where the removed heavy metals are trapped and concentrated in compartments before they reach the electrodes and potentially interrupt the electric field. The five compartment set-up may also be used if e.g. chloride is present in the system, to avoid negatively charged chloride ions to reach the anode, where it may be oxidised to gaseous chlorine.

### 5.2 Middle compartment

The polluted material is placed in the middle compartment, and if needed covered with a liquid phase (e.g. water) to ensure full contact with the membranes and thereby an even distribution of the electric field. This is the case with wood chips. In the case of a fine particle material, it may instead be saturated with the liquid prior to loading of the cell. This is the case in the traditional soil remediation set-up (*Ottosen et al. 1997, Hansen et al. 1997*) and was also used in the remediation of CCA-treated wood as sawdust (*Ribiero et al. 2000*). The use of a stirred system has proven beneficial in the remediation of fine particle materials like fly ash (*Pedersen 2002*), harbour sediments (*Nystroem et al. 2004*) and also soil (*Ottosen 2003*). In this system the polluted material is a slurry with a L:S ratio of 4 to 8 instead of merely saturated with the liquid. In order to keep the particles in suspension a stirred system is used.

In the case of CCA-treated wood as wood chips stirring was not used and is considered not relevant due to the larger size compared to fine grained particles and consequently looser packing of wood chips in the cell.

### 5.3 Current

The current strength during EDR is also a parameter that has to be optimised for the different materials. The removal rate of the heavy metals may increase with increasing current density. In remediation of soil it was found that doubling the current resulted in doubling of the removal rate (*Ottosen et al. 1997*). However there will be an upper limit and above this point, current is merely wasted without the removal rate being

increased. The removal rate may even be decreased when the upper limit is bypassed. In a loamy sand soil with low carbonate content, the upper limit was found to be between 0.3 and 0.5 mA/cm<sup>2</sup> (*Ottosen et al. 2000*). In stirred systems the upper limit for fly ash is above mA/cm<sup>2</sup>, and in harbour sediments it is above 0.6 mA/cm<sup>2</sup> (*Nystroem et al. 2004*)

For remediation of CCA-treated wood the upper limit was found to be between 0.4 and 0.8 mA/cm<sup>2</sup>

## 6. Scale up

In the process of scaling up the remediation, the setup often has to be optimised again since a direct scaling up rarely is feasible. In the laboratory the set-up is cylindrical. This is mostly due to practical reasons and it is no problem to handle the cylinders in this scale. However in the process of scaling up, a box is more convenient for practical and financial reasons. The loading and unloading of maybe hundred of kilograms polluted material into and out from the middle compartment of a EDR set-up is manageable when an open box is used, but unrealistic when a cylinder is considered. The fact that the amount of material is increased dramatically also makes it evident to consider the actual loading and unloading. What may be done in the laboratory with the use of hands and a small spoon may require shovels and special equipment in larger scale.

In the case of up scaling the remediation of CCA-treated wood from laboratory scale to a 2 cubic metre pilot scale, the wood chips was placed in plastic nets before they were loaded into the plant. When the wood was dry each net weighed about 6 kg and when wet (after soaking and EDR) the weight had increased to more than twice the dry weight. The use of nets made the handling of the wood much easier and the weight of each net was deliberately limited to make it possible for one man to load and unload the wood. Nets of polyethylene were chosen to ensure that the wood could stay in the nets in case of incineration of the remediated wood, since polyethylene can be incinerated without complications.

### 6.1. Electrode distance

In laboratory scale the middle compartment is normally less than 20 cm long and this distance also represent the longest distance the ions have to move before being collected in the electrode compartments. It is evident that the electrode distance may influence the remediation rate and therefore it is advisable to make it possible to vary this distance in the pilot plant.

In the pilot plant designed for remediation of CCA-treated wood it was possible to vary the distance between the electrodes from a minimum distance of 30 cm to a maximum distance of 3 m. This was done by designing the electrode compartments as

mobile units that could be placed on ribs in the pilot plant. The ribs were placed with 30 cm intervals. This also made it possible to remediate from approximately 50 kg to 500 kg wood at a time.

The minimum distance between the electrodes should be considered for each material. The distance of 30 cm chosen for wood was similar to the distance in laboratory experiments and the loading of the plant was manageable. A shorter distance may be beneficial in the case of other materials and should be considered when the pilot plant is developed.

## 6.2. Collecting units

Another way to shorten the distance the ions have to travel before being captured, but without having to shorten the electrode distance, is to place collecting units between the electrode units. The collecting units resemble the electrode units, but without the electrode. The collecting unit was separated from the wood in the middle compartment by an anion exchange membrane to one side and a cation exchange membrane to the other side. When ions passed into the units they were trapped due to the arrangement of the membranes. In the remediation of CCA-treated wood collecting units were placed every 30 cm and effectively shortened the way the ions had to travel before being collected.

## 6.3. Membrane area

Since the remediation rate increases with increasing current, until the limiting current density is reached it is important to ensure the largest possible membrane area. In the laboratory set-up the membranes cover the full area available between the middle compartment and the electrode compartments. The same is true in the pilot scale designed for remediation of CCA-treated wood. Here the membrane area was approximately 1m<sup>2</sup> and covered the full area apart from a small frame that was necessary to mount the membranes on and for assembling of the units.

In remediation experiments with no additive, e.g. where the water splitting at the anion exchange membrane is responsible for the acidification of the middle compartment environment, the membrane area may be of more importance, since a large membrane area will increase the area where the water splitting may take place.

# 7. End products

One of the advantages of EDR is that it has the potential of avoiding new waste fractions that may be created due to the process.

The heavy metals are removed from the material into liquids from where they may be recovered by electro-deposition or precipitation (*Hansen 2000*). The material that is no longer polluted may be reused or disposed without complications. In some cases

a recovery of the heavy metals may not be beneficial from an economic point of view and instead waste reduction may be obtained by precipitation of the heavy metals into stable compounds that may be disposed.

In the case of CCA-treated wood the liquids are proposed reused in the industry after optimisation or recovered and reused otherwise in the industry (*Christensen et al. 2004*). After removing all the arsenic and at least part of the copper and chromium, the wood may be burned and thereby utilising the energy resource of the wood.

The aim of avoiding of new waste problems must also be kept in mind when a potential additive is considered.

It is advisable to use the additives that are considered the least harmful to the environment. Even though most of the additive can be removed from the process liquids after remediation it is plausible that a fraction of the additive will be present in the remediated material that is being reintroduced into the environment, e.g. as remediated soil. Additives like mineral acids and small organic acids may not be considered as harmful to the environment as e.g. EDTA that is a strong chelating agent.

## 8. Conclusion

The process of optimising the EDR method to remediation of CCA-treated waste wood yield several experiences that may be of general interest when other heavy metal polluted materials are considered for EDR.

In figure 1 a procedure for optimising EDR to a polluted material is shown in principle.

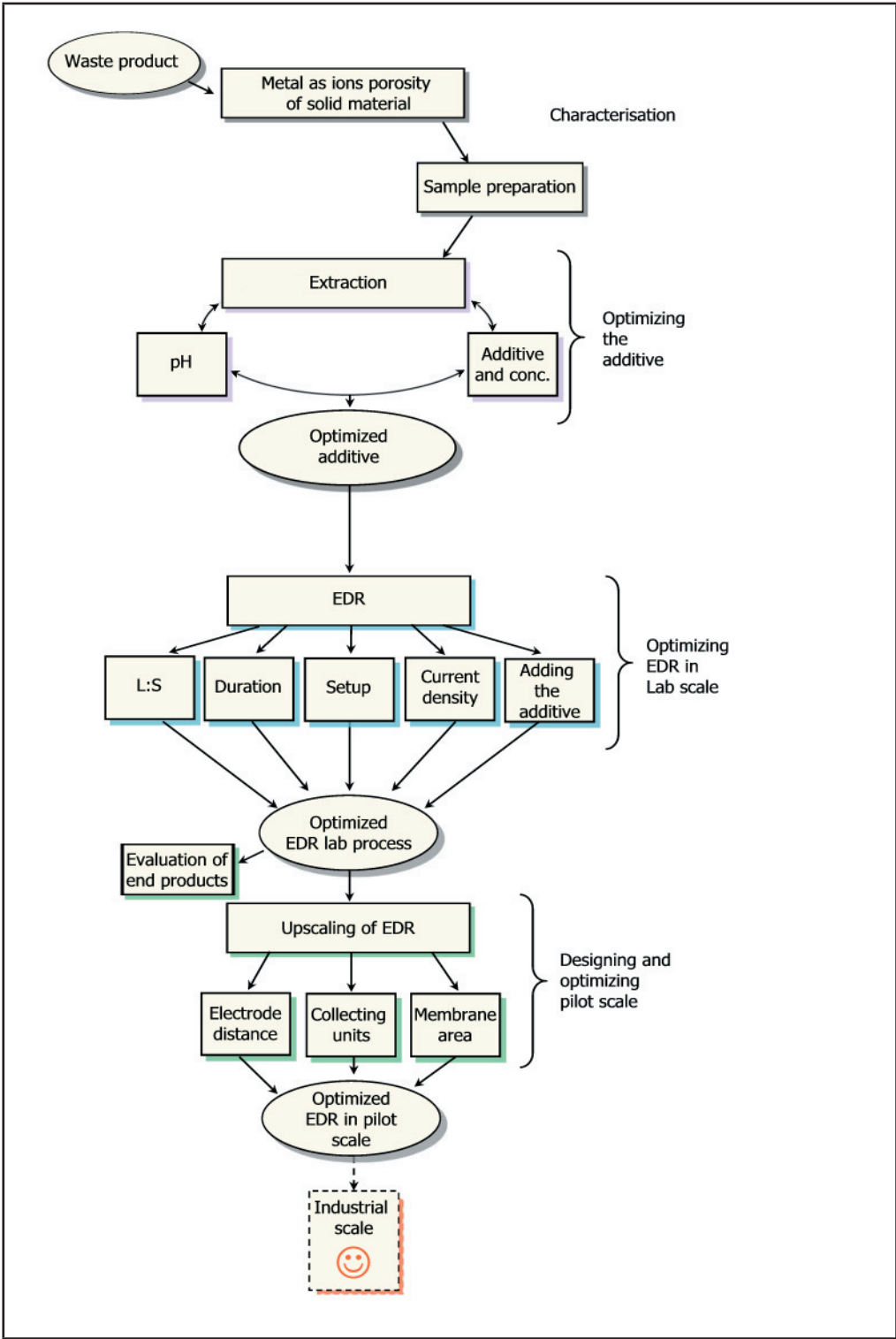
First of all a suited material for EDR is a liquid or a porous material with the heavy metal contamination present as ions. The material may be prepared to some degree (e.g. size reduced or sieved) before remediation if necessary. Initially extraction experiments are made to locate a suited additive and pH. If no knowledge of the form of pollution is known, extraction experiments may also reveal if the pollution is ionic (can be extracted). The additive is chosen with the possibility of reusing the material afterwards in mind.

EDR experiments are done in order to optimise the process with regard to current density, choice of setup (three- or five-compartment systems, with or without stirring), liquid to solid ratio, duration of experiment and the role of the additive (initial soaking or during use).

When the process is optimised in laboratory scale, the up scaling of the process may begin, as well as the evaluation of the end products. Since up scaling to pilot scale may be seen as an important step towards industrial scale remediation, the up scaling may provide valuable information regarding the feasibility of EDR as a remediation

method for the material in question. In a pilot plant parameters like electrode distance, collecting units and membrane area may be optimised, as well as the possibility of increasing the size fractions of the material (like larger wood chips).

In order for EDR to be an effective alternative to e.g. land filling, the costs of remediation should be kept as low as possible. This is to be kept in mind when processing of the material, choice of additive and the possibilities for reuse of the remediated materials are considered.



**Figure 1:** Schematic presentation of a procedure for optimisation of EDR to a polluted material.

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## Overall Conclusion

The main part of the thesis was dedicated to developing the electrodialytic remediation method for treatment of CCA-treated waste wood. The method was investigated both in laboratory scale and in pilot scale and with promising results.

The most optimal experimental conditions were dual soaking in phosphoric acid and oxalic acid followed by electrodialytic remediation (EDR). During remediation only water was used in the middle compartment. In the laboratory this resulted in removal of 92% Cu and 83% Cr and final average concentrations in the wood of 102 ppm Cu and 232 ppm Cr. In the laboratory 70 g wood chips was treated.

In pilot scale similar experimental conditions with wood from the same (mixed wood) fraction as in laboratory scale also showed good results. Final average concentrations of 163 ppm Cu, 252 ppm Cr and less than 43 ppm As was obtained in 97 kg wood.

Both spruce impregnated by sap displacement in 1962 and a mix of different waste wood fractions as it could appear in reality was investigated. The treatability of spruce and pine may differ due to difference in wood structure and impregnation method, however the CCA fixation products are presumed to be similar in the two species and they seem possible to remove by EDR.

The influence of several parameters on the remediation success was investigated.

SEM analyses of the distribution of Cu and Cr in CCA-treated wood before and after EDR did not reveal any particular bonding that was not affected by EDR. CCA was found in both tracheids and rays, but after partly remediation of the wood both Cu and Cr was found in visible deposits on the surfaces of the cells. There was no indication that these deposits could not be removed with further remediation.

Different additives was tested and the best suited additive was not the same for Cu and Cr. Phosphoric acid proved most suitable for Cu and oxalic acid proved to be suited for the removal of Cr. The combination of phosphoric acid and oxalic acid also removed As. Since this is most commonly an anion it is not expected to complex or precipitate with the additives. The main factor to ensure remediation of As may be the mobilization/removal of Cr, since As is predominantly present in the wood as chromium arsenate. Locating a single additive that was ideal for both Cu, Cr (and As) would be ideal, but this was not accomplished. Instead dual soaking was used.

Soaking of the wood prior to EDR proved very efficient. The easy removable CCA was removed without current. By introducing the additive into the wood before EDR was applied the total amount of additive was significantly reduced as opposed to using the additive directly in the EDR setup.



The process could be up scaled from 70 g wood chips in laboratory scale, to 97 kg with same high removal of Cu, Cr and As. Further up scaling resulted in lower removal of Cu and Cr. It is believed that the process can be further optimized by introducing a stronger power supply. The power supply available for the pilot plant experiments could not maintain the optimum current density of approximately 0.8 mA/cm<sup>2</sup> for removal of Cu and Cr from the middle compartment into the electrolytes.

The up scaling to pilot plant also made it possible to investigate the influence of the size of wood chips on the remediation efficiency. There was a clear tendency towards increased removal with decrease in wood chips size. It may be possible to overcome this by ensuring total saturation of the larger wood chips, e.g. by vacuum soaking of the wood.

In evaluation of the end products both the influence of oxalic acid on the strength of the wood and the ability to reuse process liquids with removed CCA was investigated. It was concluded that the use of oxalic acid has no influence on the bending strength of the wood, but some degree of pretreatment of the process liquids was needed before use for impregnation of new wood. The problems was presence of additive and the fact that Cr was present as Cr(III) in the process liquids, but should be Cr(VI) in the CCA preservative solutions.

Other reuse options may be more suitable and maybe the metals need to be separated before further use.

The results and experiences that were gained during the above optimization process may serve as useful background knowledge when other materials are considered for EDR.

Knowledge about the material and pollutant may reveal if the pollutant is likely to be transformed into ions, as a successful treatment by EDR depends on this factor. This knowledge may be obtained by extraction experiments.

Finding a suitable additive is a key parameter and even though a single additive is preferred, this may not be available if a mix of pollutant is to be removed.

Parameters like current density, EDR set-up, use of soaking and type of additive must be evaluated based on the individual material.

Parallel to the present Ph.D the EDR method has been expanded from remediation of soil, to harbour sediments and fly ash by other members of the electrochemical remediation team and with very good results. The experiences gained in this Ph.D and from other members in the electrochemical remediation team with other products, may be used as a starting point for evaluation and testing of new materials.

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